Fermented Beverage Production

SECOND EDITION



Edited by

Andrew G. H. Lea

and

John R. Piggott

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Second Edition

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Preface

We were encouraged by the reception given to the first edition of this book. We had felt the need for a single volume to cover the topic of fermented alcoholic beverages in their present-day diversity, and most of our reviewers seemed to agree with us.

In this second edition the original chapters have been variously updated. We have tried to address some of the shortcomings of the previous book, in particular by including new chapters on rum, on sparkling wine production, and on a range of South American beverages. We hope this will to some extent console the reviewer who described us as 'depressingly Eurocentric'!

A single volume like this one can never be all things to all its readers. For lack of space and lack of authors, it does not cover fermented milks, mead, or tropical beverages such as palm and rice wines. Nor can it be a quality control or an analytical laboratory manual for the beverage industry. For those, the reader must look elsewhere. Our aim has been to provide an authoritative technical snapshot of the major alcoholic beverages in the early years of a new millennium—if we and our contributors have succeeded for the majority of our readers, then we shall be happy!

As with the first edition, we thank our authors for their hard work, and the publishers for their forbearance and patience! Productions of this sort are a team effort and we are grateful to everyone, whether named or not, who has contributed to this volume.

Andrew G.H. Lea
John R. Piggott, 2003

From the preface to the first edition

The production of fermented alcoholic beverages is nowadays a technically sophisticated business. Many people outside it, however, even if they are familiar with the food industry overall, fail to appreciate just what advances have been made in the last twenty or thirty years. In part this is due to the blandishments of advertising, which tend to emphasise a traditional image for mass market promotion at the expense of the technological skills, and in part due to a lack of readily available information on the production processes themselves. This book attempts to remedy the balance and to show that, far from being a quaint and rustic activity, the production of fermented beverages is a skilled and sophisticated blend of tradition and technology.

We have chosen to organise the book principally by individual beverages or groups of beverages, with the addition of a number of general chapters to cover items of common concern such as fermentation biochemistry, filtration and flavour. While we have tried to eliminate excessive duplication of information, we make no apologies for the fact that certain important aspects (e.g., the role of sulphur dioxide in wine and cidermaking) are discussed on more than one occasion. This only serves to underline their importance and to ensure that each chapter is moderately self-contained.

We have deliberately chosen an international range of authors and in many cases we specifically went to the New World, to reinforce the message that technology and quality can and do

go hand in hand. The fermented beverage industry worldwide has profited enormously from the interchange of information between 'new' and 'traditional' production areas and product types, to their continuing mutual benefit. We hope that this book will play its part in this interchange and that technical staff already within the industry will find it a useful source of information between one set of covers, perhaps providing new ideas from fields which are not directly their own. We hope for a much wider readership, too, in colleges and research institutions, in the technical departments of the retail trade and indeed from anyone who seeks an overall scientific understanding of the modern production of fermented beverages.

Finally we thank the contributors for their work and the publishers for their patient support and encouragement. If we have been successful it is due to their efforts; if we have failed the responsibility is ours alone.

Andrew G.H. Lea
John R. Piggott
1995

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1

Production of Fermentable Extracts from Cereals and Fruits

A. Paterson, J. S. Swanston and J. R. Piggott

INTRODUCTION

Alcoholic beverages are consumed primarily because ethanol forms a significant component. The principal organisms in most alcoholic beverage fermentations, yeasts, are able to produce ethanol primarily through metabolism of the low-molecular-weight sugars that can be transported into the cell cytoplasm. Thus, in production processes utilizing cereals or tubers, fermentations must be preceded by a depolymerization of storage polysaccharides and proteins yielding the sugars and amino acids that can be utilized by the microorganism. In cereals, storage polymers are enclosed by plant cell walls into compartments that limit losses through hydration, enzymic and also microbial attack. As these cell walls are also predominantly formed from polysaccharides, their breakdown yields further sugars: hexoses, which can be metabolized by the dominant yeast *Saccharomyces cerevisiae*, and pentoses that are not metabolized by *S. cerevisiae* but are frequently catabolized by lactic acid bacteria.

Since cereals represent the major source of storage carbohydrates, and the cell walls of monocotyledonous plants are different from those of dicotyledons, this chapter will focus largely on how fermentable solubles are produced from cereal crops. Since in Europe and North America, barley and wheat are the dominant cereals, these will be considered in depth although special features of maize and rice will also be discussed. Malting of barley will be discussed because the activity of enzymes derived from this source is central to production of beverages from cereals.

The major cereal storage carbohydrate is the polysaccharide starch. In cereals starch is present in granules, structures that are associated with proteins. Both starch and protein represent storage reserves for plants that can be depolymerized at the time of germination. In cereals, storage is effected largely in a specific compartment, the endosperm, during grain development and at maturity enzymic activities in these storage tissues are low. When required, polymers are broken down to yield solubles that can diffuse to the centers of metabolic activity, the embryo or germ. Man has learned how to exploit this depolymerization by establishing by empirical means how to elicit this solubilization and effect a subsequent aqueous extraction without losing

excessive amounts of carbohydrates in metabolic activity. During the industrial germination process, malting, there are profound changes in the grain structure, largely related to degradation of polymers in the starchy endosperm by endogenous enzymes. Solubilization and depolymerization of carbohydrates and proteins continues during and following extraction of malted cereals with hot water. However, effective breakdown of starch requires disruption of the granules in which the polysaccharide is preserved in an inert form in the endosperm. Therefore a solubilization or the gelatinization process is used to enhance enzymic access to hydrolyzable bonds. This gelatinization, however, requires the use of elevated temperatures that denature the enzymes responsible for depolymerization of storage and cell-wall polymers. Therefore, in industrial practice exogenous enzymes may be added to supplement or replace activities lost through the elevated temperatures needed to ensure maximal solubilization of potentially fermentable material. The aqueous extraction of cereals using hot water is known as mashing and is central to the economics of alcoholic beverage production. Achieving the correct balance of appropriate cereals at this stage in the process is important in achieving optimal product character and yield of ethanol. In addition to polysaccharides, amino acids and lipids extracted during mashing can act as precursors for reactions important in yeast metabolism, beverage flavor and character.

This chapter will seek to review the nature of the polymers that will yield the fermentables and the processes by which low-molecular-weight compounds are formed and extracted. Production of beers, whiskies and neutral spirits untilize similar biochemical pathways for cereal polymer degradation; certain oriental beverages, however, may utilize alternative processes.

Structure of Cereals

Grain Development

Cereals produce both male, pollen, and female, ovary, sexual structures. In monocotyledons the pollen grain, following release from the anther, germinates on the stigma to form a pollen tube. This tube, which contains two haploid male nuclei, penetrates the embryo sac and one nucleus then fuses with the haploid female nucleus to form the diploid embryo (Palmer, 1989). In barley, each haploid nucleus contains seven chromosomes and the final diploid nucleus contains fourteen. The second male nucleus fuses with two polar embryo sac nuclei, yielding the endosperm which in barley is triploid, with 21 chromosomes.

The outer layer of pericarp of the embryo sac becomes green as photosynthetic pigments are laid down. Grain development proceeds with division of cells in the endosperm, which terminates with the inner cells ceasing to divide before those in the outer layers. Following completion of division, the endosperm cells proceed to synthesize starch and swell. During this time the outer cells differentiate to form the aleurone, which in the mature grain will not contain starch but will produce the enzymes essential for mobilization of the endosperm storage polymers. The aleurone layer in barley is generally three cells deep, but in wheat, maize and rice it is only a single cell in depth. In barley, the aleurone contains > 90 % of the myo-inositol hexaphosphate or phytic acid in the grain. This source of phosphorus is also an important influence on the pH of the extraction liquor. The barley aleurone is also rich in lipid (*ca.* 20 % by weight).

The developing grain is surrounded by the tissue that will form the husk. In barley this is generally 10 % by weight of the final grain. In wheat and rice, the husk becomes detached during threshing. The cereal husk contains both silica and lignin which increases resistance to mechanical damage and acts as a barrier to microbial attack. The husk, derived from parental leaf tissue, is attached to the pericarp, an outer epidermal layer of cuticular material originating from the ovary wall. This pericarp is impervious to carbon dioxide and plant hormones, such as gibberellic acid. Abrasion of this layer can lead to major changes in the metabolism of the cells in the grain.

Lying between the pericarp and the aleurone layer covering the endosperm is the testa, or

testa-nucellus. In the mature grain this can be observed to have two cuticular layers which are rich in lipids. In certain barley cultivars, this tissue is also pigmented. These layers appear to be semipermeable and incomplete, in that the complete endosperm is not covered.

The fundamental structures of barley and wheat grains important in production of beverages are summarized in Figure 1–1a, b. For a detailed consideration of barley grain structure the review of Palmer (1989) should be consulted.

The Cereal Endosperm

The component of cereals central to the interests of the brewer or distiller is the starchy endosperm. In the mature barley there are three distinct zones in this tissue, differentiated by elongated cells, larger purse-like cells or the smaller cells that lie immediately below the aleurone. It has been estimated that the typical barley endosperm contains approximately 2.8×10^5 cells (Cochrane and Duffus, 1981), whereas that of rice contains 1.8×10^5 and wheat only 1.12×10^5. In barley adequate expansion of endosperm cells is a prerequisite for synthesis of starch granules suitable for malting. Failure of this process may be a problem in adverse growth or environmental conditions.

Cereal Storage Polymers

Starch

Starch is a homopolymer of D-glucopyranose units linked primarily by α-(1-4) bonds, in contrast to cellulose and mixed β-(1-3)(1-4)-glucans, formed from β-linked D-glucose residues. Starch polymers can be considered to have the disaccharide maltose as the repeating unit. This is important because the starches are homopolymers which can, by virtue of the repeating nature of their structure, form crystalline regions through intermolecular hydrogen bonding be-

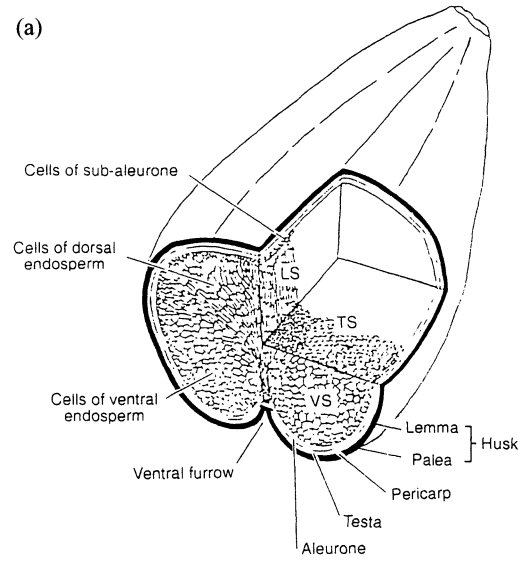


Fig. 1–1(a)

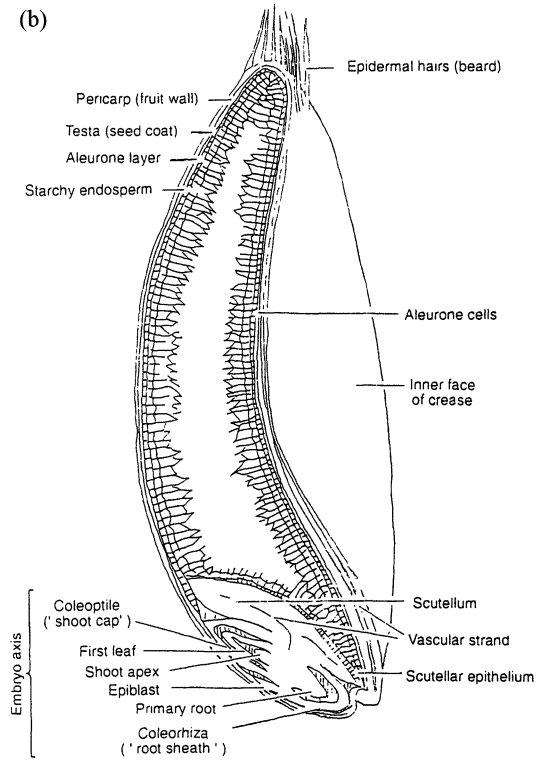


Figure 1–1 Fundamental structure of (a) barley and (b) wheat. LS, longitudinal section; TS, tranverse section; VS, vertical section. (Adapted from Palmer, 1989; Barnes, 1989.)

tweeen α-glucan chains. However these polymers may also exist as soluble components, depending upon their structure and molecular weight, and this soluble form will be dominant following gelatinization.

Starch was initially considered a single polysaccharide of complex structure but Meyer and Bernfeld (1946) showed that two fractions, amylose and amylopectin, with differing properties could be discerned. In both the polymers the predominant bond is the α-(1-4) linkage, but in amylopectins α-(1-6) bonds are also observed and this branched structure modifies the property of the polymer.

Amylose

Most plant starches contain between 15 and 25 % amylose, present as crystalline and amorphous forms in endosperm granules. Amorphous amylose can leach from granules following hydration by water and the soluble amylose chains can adopt either helical structures or parallel alignments arizing from reformation of intermolecular hydrogen bonds. This latter structuring results in spontaneous precipitation in aqueous solutions, referred to as retrogradation. Iodine ions fit into amylose helices in solution, forming the dark blue coloration that forms the basis of the most popular quantitation (Morrison and Laignelet, 1983). In cassava starch 50–75 % of amylose is soluble (Raja *et al.*, 1982). Amylose polymers are considered to contain up to approximately 10^5 glucopyranose units. Although early studies considered that amylose polymers were linear, it is now clear that there are a number of branch points in these molecules and in maize amylose (degree of polymerization (DP) 930–990) it is reported that there are, on average, 5.3 chains per molecule (Takeda *et al.*, 1988).

Amylopectins

Amylopectins are markedly higher in molecular weight than amyloses and exhibit more complicated branched structures. The α-(1-4) bond forms *ca.* 94–96 % of intermonomeric linkages (Banks and Greenwood, 1975) with the residual bonds being α-(1-6). The result is families of molecules with chains of approximately 20–24 monomers, interlinked to form branched structures. These chains can be discriminated into A, B and C types where only the C contains the free reducing group. With both A and B chains, the potential reducing end (C-1) of the chain is bonded to the C-6 position of a glucose residue on a further B or a C chain. From the model of French (1972) in which clusters of A together with certain B chains form crystallites linked by amorphous B chains (Figure 1–2), the complexities of amylopectin structure can be discerned. Since both A and B chains can also be discriminated into short (DP 11–25) and long (DP 52–60) types, considerable scope for structural variation exists. As relationships between chain types and lengths are complex and influenced by growth temperature, genotype and species, it is generally accepted that amylopectin polymers have a cluster structure that will vary in relation to their origin (French, 1984).

Starch Granules

Starch is synthesized in plant cells within subcellular organelles separated from the cytoplasm by double membranes. In cereal endosperms these are amyloplasts, but in dicotyledons starch may also be found in chloroplasts and chloroamyloplasts. In certain cereal amyloplasts, such as those in wheat and barley, a single type 'A' granule is formed initially but subsequently a second smaller type 'B' granule appears. Therefore, in mature wheat grains, two distinct populations of granules are observed, the larger type A (20–30 μm) and smaller spherical type B (2–10 μm). In early development the type A are spherical but with maturity these granules become elongated and flattened as a result of the preferential accumulation of starch in the equatorial plane. The result is a spheroid with a distinct equatorial groove (Figure 1–3). In maize, starch granules are round or angular, whereas potato starch granules are large and oval with eccentric hili.

Both the proportions of amylose and amylopectin and the shape of the starch granules are a function of the plant genotype. Crystallinity in starches is predominantly a property of the amylopectin fraction and is reflected as characteristic patterns obtained in X-ray diffraction studies

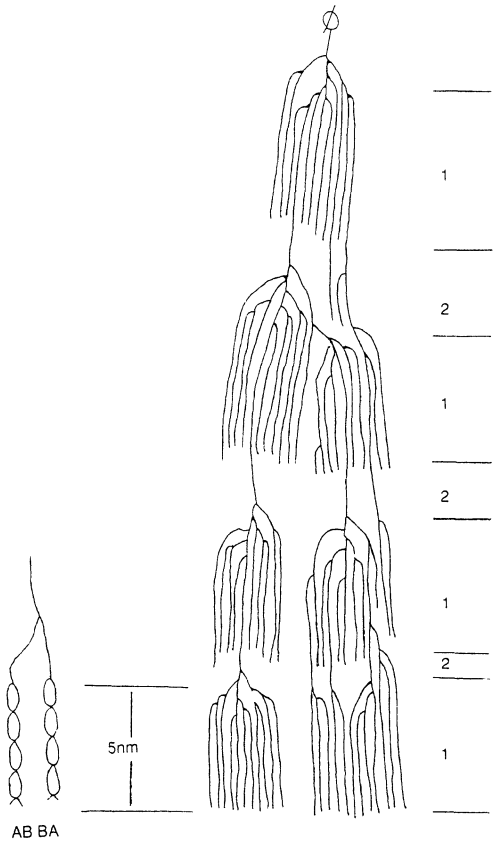


Figure 1–2 Cluster model for starch amylopectin structure. 1, crystallin; 2, amorphous regions of amylopectin. (Adapted from French, 1972.)

(Hizukuri, 1969; Hizukuri, 1985). On the basis of such approaches, structures have been divided into type A, typical of cereal starches; type B, typical of tubers and retrograded amylose; and type C, observed with smooth pea and legume starches. Of these patterns types A and B appear to be distinctly different, with type C being an intermediate form. Starch granules show birefringence when illuminated with polarized light implying there is a high degree of molecular order. This order is confirmed in light and electron microscopic studies, in which sectioned starch granules appear to contain 'growth rings' that radiate from the hilum, and within these rings fine lamellae about 100 nm thick can be discerned.

When starch granules are heated in excess water, the polymers undergo an irreversible dissociation of α-glucan chains during which hydration disrupts the intermolecular hydrogen bonding. This is accompanied by granule swelling and carbohydrate leaching. This process, gelatinization, is important in production of fermentable carbohydrates from cereals since without it a large part of the polysaccharides will be lost to the process. Swelling begins in the amorphous regions within granules and progresses from the hilum to the periphery. The amorphouse regions appear to promote breakdown of the crystallite regions either by stripping of glucan chains from the double helices of amylopectin (Biliarderis *et al.*, 1980) or by melting of these regions in the polymer (Evans and Haisman, 1982). The amorphous regions of starches tend to behave rather differently from crystallites and pass through a glass transition. The influences of differences in structure as such that individual starches will have characteristic temperatures for gelatinization. These can be determined as the temperature at which there is a loss of both birefringence and X-ray diffraction patterns. Certain starches show linear increases in volume during gelatinization whereas in others, such as in rice, the process occurs as two distinct stages. When starches swell the polymers show major increases in surface area accessible to water-soluble molecules such as dyes and enzymes. During swelling amylose may also be leached from the granule. Thus the hydration effected in gelatinization is a prerequisite for enzymic depolymerization of starches, saccharification. The literature that describes starch gelatinization is abundant (Biliarderis *et al.*, 1986). It is perhaps sufficient to indicate that the underlying science is complex and the process markedly influenced by the presence of salts, lipids and many organic compounds as well as degree of damage to starch granules, the pH and the presence or absence of amylolytic enzymes.

Starch Lipids

Typical commercial starches are between 97 and 99 % polysaccharide and up to 0.9 % protein. Normal starches appear to contain 0.1–

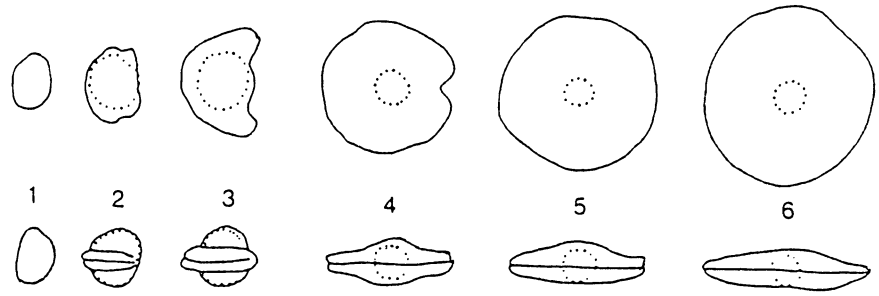


Figure 1–3 Developmental stages of wheat A-type granules: top row, plan view; bottom row, side view. (Adapted from Evers, 1974.)

0.9 % protein whereas high amylopectin or waxy starches have < 0.4 % protein. Nonwaxy starches contain approximately 1 % lipid and the waxy starches somewhat less. Lipids present in starches have been divided into three components: internal, starch-surface and non-starch. Non-starch lipids in cereals are derived largely from the encapsulating spherosomes and other membrane components. In most cereals, this lipid component consists predominantly of triglycerides and diacylphospholipids. In maize, rice and sorghum, however, as the endosperm matures lipolysis yields both free fatty acids and monoacyl lipids which can be recovered from starch derived from these cereals. Starch surface lipids appear to be derived primarily from the non-starch fraction and are, at least partially, present as amylose-lipid complexes on starch granule surfaces. Surface lipids have, however, a higher content of monoacyl lipids than the non-starch component.

The major part of the true internal starch lipids are lysophospholipids, being approximately 70 % lysophosphatidyl choline, 20 % lysophosphatidyl ethanolamine and the residue predominantly lysophosphatidyl glycerol. In barley and wheat, internal lipids are > 90 % lysophospholipids. This lipid class forms only approximately 70 % starch lipids in rice, 55 % in sorghum and 40 % in maize. The residue is essentially free fatty acids of which 40–60 %, are saturated and the residue *cis*-unsaturates with linoleic being more abundant than oleic or linolenic acids (Morrison, 1988). Such monoacyl lipids may also form inclusion complexes with amylose (Morrison, 1988) and this may relate to the starch behavior. The lipid content of both wheat and barley starch granules increases with maturity and is inversely related to granule size (Morrison and Gadan, 1987; McDonald and Stark, 1988). In certain cereal mashes, starch lysophospholipids may represent a source of phosphorus for the yeast in fermentation.

Storage Proteins

The storage proteins are deposited in the cereal endosperm, shortly after fertilization, in discrete subcellular bodies. The storage proteins assume a more amorphous form as the grain matures and in the mature cereal form a matrix in which the starch granules are embedded. Cereal proteins are fractionated on the basis of solubility in salt and aqueous ethanol solutions. In barleys, the major storage proteins are the hordeins and glutelins, both of which have high contents of glutamine and proline. The total protein content varies between 8 and 13 % on a dry weight basis; of this 70 % is found in the endosperm and 20 % in the aleurone and scutellum. A further 5 % has been reported to be a component of the cell walls. The salt-soluble cereal proteins are the albumin and globulin fractions, 3–5 % and 10–20 % total protein, respectively. These fractions include the enzymes that will participate in the modifications of the endosperm storage polymers central to malting and mashing.

The relationship between storage proteins and starch in barley is complex and, as suggested by Palmer (1989), perhaps central to malting quality. It is clear that protein and starch contents are inversely related. Moreover during grain development, protein and starch matrices in the endosperm can take different forms, with the extremes being 'mealiness' and 'steeliness'. Reductions in protein content and number of small starch granules leads to mealiness which results in increases in water-free spaces in the endosperm. In contrast, in 'steely' endosperms there is reduced access for the water required to effect hydration, and thus limited opportunities for enzymic attack on the storage polymers.

In wheat, endosperm proteins are generally divided into five fractions on the basis of the classical extraction procedure of Osborne (1907): albumins, globulins, gliadins, glutenins and 'residue' proteins. The gluten that is important in forming bread is generally a mixture of glutenins, gliadins and 'residue' proteins. In production of neutral spirit from grain, this protein fraction can be recovered as a valuable by-product and sold on to the food industries. The important endosperm proteins in maize, the zeins, are related to wheat gliadins and barley hordeins (Table 1–1; Utsumi, 1992). Zeins appear to be very compact molecules with high contents of glutamine, leucine, alanine and proline but are deficient in lysine. Certain zeins are also rich in methionine. The dominant storage proteins of rice are the glutelins (*ca.* 80 %), related to the glutenins in wheat. In each cereal the solubilities of storage proteins can be related to the nitrogen compounds available for yeast metabolism in the final aqueous extract. Although in most cases cereals other than barley are not used in malting, maize, rice and wheat are treated with microbial enzymes or malts, following cooking to induce gelatinization of starch, in production of grain spirits and in many beers.

Cereal Lipids

In barley, lipids represent approximately 3.5 % of the grain on a dry weight basis, predominantly

Table 1–1 Storage proteins in cereals

(a)

Barley endosperm proteins	*Hot 70% ethanol extract (%)*	*Hot 50% propan-1-ol extract (%)*
Hordein	35	50
Glutelins	35	20
Albumins	10	10
Globulins	20	20

(b)

Prolamins	*Type*	*Wheat*	*Barley*	*Rye*
Sulphur-rich prolamins (30–50 kDa)	Monomers	α/β-Gliadin	γ-Hordein	γ-Secalin
	Aggregates	Low-molecular-weight glutenin subunit	B-Hordein	
Sulphur-poor prolamins (44–80 kDa)	—	ω-Gliadin	C-Hordein	ω-Secalin
High-molecular-weight prolamins (60–90 kDa)	—	High-molecular-weight glutenin subunit	D-Hordein	High-molecular-weight Secalin

Adapted from Palmer (1989) and Utsumi (1992).

consisting of triglycerides in the aleurone and spherosomes within the embryo. A minor percentage consists of endosperm phospholipids, part of which are associated with the starch granules. Barley lipids are dominated by the unsaturated linoleic (52 %) and oleic (28 %) acids with the saturated palmitic acid being around 11 % of the total. During germination of barley, increased lipase activity is observed. Although this leads to rapid lipid hydrolysis, kilned malted barley contains *ca.* 3 % lipid suggesting metabolism of this storage reserve is limited. The major part of this lipid also appears to be retained within malt during subsequent mashing processes, although both temperature of extracting water and mechanical agitation can influence the extent of this extraction.

In wheat the dissected germ may contain 25 % lipid of which approximately 75 % are triglycerides with the residue being non-polar lipids and phospholipids. Approximately 70 % of wheat fatty acids are unsaturated. In general the importance of lipids in alcoholic beverage production is not related to ethanol formation but rather as precursors for important classes of flavor-active compound, such as ketones, and in off-flavor development.

Cereal Cell Walls

Basic Structure

The cereal cell wall is important because these structures limit access of enzymes and water required to effect the depolymerizations that will generate the fermentable solubles. In many processes utilizing barley, the cell-wall material of the husk is utilized as a primary filter-aid after extraction of the solubles in mashing. Cell walls in the endosperm will vary in structure depending on the position of cells within the tissue. Although in the barley cultivar Triumph it has been reported that the cell wall is 2 μm thick (Palmer, 1989), other authors (Wischmann and Schildbach, 1987) have suggested that the presence of a large number of small cells in the endosperm has more influence on extraction of the endosperm polymers than wall thickness.

Cereal cell walls contain both carbohydrate and protein, although the latter is generally low, 1–6 % in barley endosperm cell walls. The polypeptides form a matrix that interacts with the carbohydrates, which can be divided into those formed from β-linked glucose residues, the glucans and celluloses, and those containing pentose sugars in varying proportions, the hemicelluloses or pentosans. The pentosans are in cereals dominated by the arabinoxylan polymers. Cereal cell-wall structure has been reviewed definitively by Fincher and Stone (1987).

More recently, Kanauchi and Bamforth (2001a) cultivated the fungus *Trichoderma viride* on a medium containing a crude preparation of barley endosperm cell walls and noted the order in which enzymes of degradation were produced. The same authors also noted the capacity of several enzymes including esterases, xylanases and arabinofuranosidase to enhance solubilization of β-glucan from the cell walls (Kanauchi and Bamforth, 2001b), although only a small proportion (up to 12 %) of the pentosan was released. From these results Bamforth and Kanauchi (2001) postulated a model for the architecture of the endosperm cell wall in which an incomplete layer of pentosan was located in the outer regions, restricting solubilization of glucan. This did not, however, preclude glucanases accessing their substrate nor, in the absence of enzyme activity, a portion of the water-soluble glucan being brought into solution. Enzyme activity, by removing all or part of the outer layer, enhanced accessibility to the glucan. The major portion of the pentosan may, however, be located in the inner part of the cell wall, possibly bound to the middle lamella (Palmer, 1989).

The time of completion of cell walls during grain development is rather varied, being nine days after fertilization in rice, 20 days in wheat and 30 days in barley. Endosperm cell walls are also thinner in rice and maize than in wheat and barley. Cell walls vary dramatically within a single grain. Barley aleurone cell walls are reported to be 65–67 % pentosan and 26–29 % glucan, whereas in the endosperm walls are approximately 20 % pentosan and 70 % glucan. Aleurone cell walls are also thicker than endosperm walls in wheat, barley and rice and consist of two distinct layers. The thinner, inner layer remains

almost intact during germination whereas the outer layer, which has a striated or lamellated appearance, is largely degraded. Following alkaline extractions, cellulosic microfibrils are evident in this outer layer. Aleurone cell walls have large intercellular wall channels that appear to allow communication between adjacent cells and may assist movement of enzymes.

Rice endosperm cell walls appear to be rather different from those in other cereals in that there are significant contents of pectins and xyloglucan, a hemicellulose not abundant in other cereals.

Glucans and Celluloses

Glucans and celluloses both consist of β-linked glucose residues but the properties of these polymers are distinctly different. Cellulose residues are exclusively interlinked by β-(1-4) bonds generating a repeating unit of the disaccharide cellobiose. Hydrogen bonding between the O-5 and the O-3′ and O-2 and O-6′ of adjacent glucose units stabilizes the linear polymer into a ribbon-like and rigid structure (Figure 1–4). These chains are thus able to align and stack, generating the elongated crystalline microfibrils which have a major structural role in all plants. Within the microfibrils, parallel chains are locked into position by intermolecular hydrogen bonding. Cellulose has, therefore, a definite crystalline structure although within microfibrils the degree of crystallinity may vary, generating regions that are more amorphous. These cellulose microfibrils represent a major structural element in cereal cell walls and form the residue remaining after alkaline extractions of cell wall material.

The glucans are a more diverse group of polymers. Both β-(1-3) and β-(1-4) linkages are abundant, and in most cereals the glucans appear as a family of polymers varying in molecular size and structure. Different fractions can be obtained on the basis of solubility in water at different temperatures, or in alkali or in chaotropic agents, such as urea. The water-soluble (1-3, 1-4) β-glucans of barley appear to consist of *ca.* 70 % β-(1-4) and 30 % β-(1-3) bonds. Although certain glucans appear to consist of clusters of two or more β-(1-4)-linked residues, separated by single β-(1-3) bonds, there appears to be no repeating structure (Figure 1–5). In certain barley cultivars, more than 10 % of the fraction of glucan that is soluble at 40 °C consists of blocks of between four and fourteen β-(1-4)-linked residues. Such polymers may behave differently from other glucans. In general, however, it is accepted that barley glucan structure is dominated by blocks of three (cellotriosyl) and four (cellotetraosyl) β-(1-4)-linked units separated by β-(1-3) linkages. An important consequence of the structure of cereal glucans is related to their average degree of polymerization (DP) of > 1000: the value for barley is considered to be on average between 1200 and 1850 residues. Aqueous solutions of cereal glucans are very viscous which may have a marked influence on beverage production processes.

Hemicelluloses

The arabinoxylans are important components of cereal cell walls although their structure and breakdown in barley during malting is not well understood.

The arabinoxylans appear to consist of linear backbones of β-(1-4)-linked xylose units, with a significant proportion of residues substituted at O-2, O-3 or both atoms (Figure 1–6). The major substituents are single α-L-arabinofuranosyl

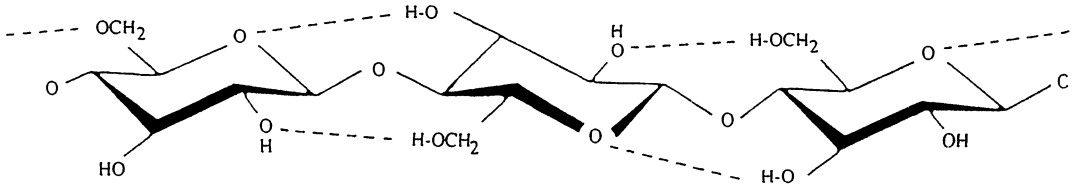
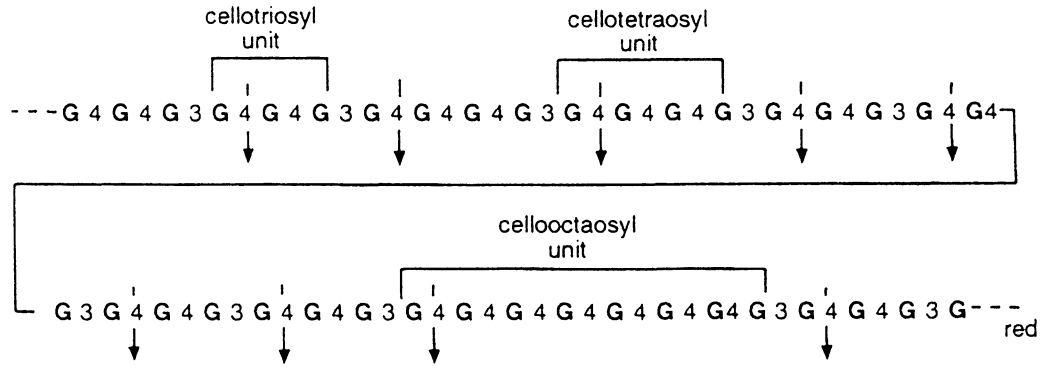
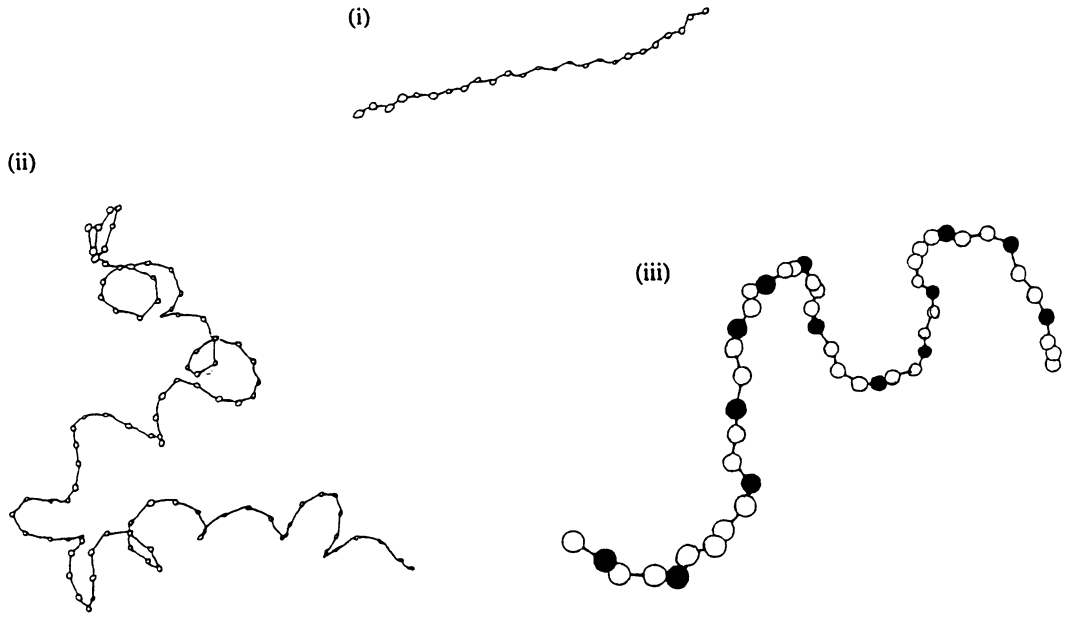


Figure 1–4 Intramolecular bonding in the cellulose β-glucan chain (from Fincher and Stone, 1987).

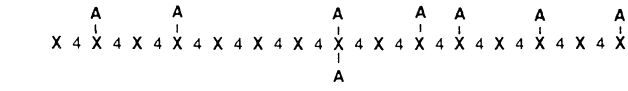


(a)

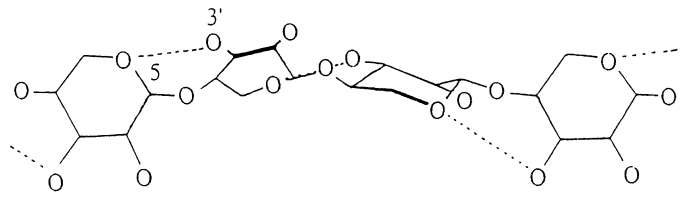


(b)

Figure 1–5 Barley β-glucan structures. (a) Distribution of linkages. G, β-glucosyl units; 4,(1-4) linkage; 3,(1-3) linkage; red, reducing end; arrows, sites of hydrolysis by β-(1-3)(1-4) glucanases. (b) Perspective drawings of computer-generated instantaneous conformations of β-glucans. (i) β-(1-4)-glucan; (ii) β-(1-3)-glucan; (iii) β-(1-3)(1-4)-glucan; closed circles, (1-3)-linked residues. (From Fincher and Stone, 1987.)



(a)



(b)

α-L-Ara*f*-(1-
4-Me-D-Glc*p*A-(1-
D-Glc*p*A-(1-
β-D-Gal*p*-(1-5)-L-Ara*f*-(1-
β-D-Xyl*p*-(1-2)-L-Araf-(1-
β-D-Xyl*p*-(1-3)-L-Araf-(1-
β-D-Gal*p*(1-4)-β-D-Xyl-(1-2)-L-Ara*f*-(1-
(or L)
4Me-D-GlcA-(1-4)-D-Xyl*p*-(1-4)-D-Gal*p*-(1-

(c)

Figure 1–6 Barley arabinoxylan structure. (a) Distribution of arabinosyl residues. X, β-D-xylopyranosyl unit; A, α-L-arabinofuranosyl unit; 4, β-(1-4) linkage. (b) Twisted ribbon conformation showing hydrogen bonding. (c) Substituents to β-(1-4)-xylon backbone. (From Fincher and Stone, 1987.)

residues, mainly linked to O-3 atoms. Single α-D-glucuronopyranosyl residues and 4-*O*-methyl esters are also O-2 linked to xylose units in arabinoxylans, and although generally these form < 2 % of residues, values as high as 9 % have been reported. Disaccharide substituents such as 2-*O*-β-D-xylopyranosyl-L-arabinofuranosyl and D-galactosyl-L-arabinofuranosyl residues are also present as minor substituents. The ratio of xylose to arabinose residues in pentosans can vary markedly, generating fractions differing in aqueous solubility. Arabinoxylans extracted with water generally have xylose-arabinose ratios of 1.4–1.5, whereas those soluble only in alkali have ratios of between 2 and 4. Arabinoxylans, as do mixed glucans, form highly viscous aqueous solutions which may produce problems particularly when wheat is used in processes such as production of grain spirits. The degree of arabinose substitutions will influence the conformation adopted by arabinoxylans and the resulting viscosity of solutions. This may be more important than the degree of polymerization, which for barley endosperm arabinoxylans has been estimated as between 7500 and 38000, and in wheat endosperms as 600–38000.

Structural features of rice endosperm xyloglucans are discussed by Watanabe (1984).

MALTING

Outline of Barley Malting

Most malts used in alcoholic beverage production are produced from barley although other

cereals are malted for production of certain speciality beers and North American spirits. This is partly a reflection of the lipids present in barley, since malting of other cereals produces distinctive lipid-derived aromas, and lipids are major contributors to formation of cereal flavor compounds through lipid oxidation. Interaction between lipids and Maillard browning reactions is also an important part of the malt flavor development during kilning (Tressl *et al.*, 1983; Eriksson, 1994).

Malting, originally a craft activity with procedures derived by empirical means, has been transformed by recent developments in technology and an understanding of the underlying science. Malts for brewing can be readily differentiated from those used in distilling as being derived from heavier grain kernels and having a more friable endosperm. Essentially grain is chosen by the maltster to meet the needs of the brewer or distiller and indeed it is becoming common in whisky production for the end-user to specify barley cultivar. Moisture and nitrogen contents will be quantified, and embryo viability and germinative capacity assessed. Viability of barley is a critical parameter and can be reduced by short-term storage at high moisture content (> 16 %), long-term storage at intermediate moisture contents (15–16 %) or elevated temperatures during drying. Viable grain may also in practice fail to germinate because of dormancy, a metabolic state that is not well understood but is important in certain cultivars (Stowell, 1986). Maltsters take care to assess such factors using micro-malting procedures.

Grain is graded and then steeped in water, with air rests to assist respiration, and allowed to germinate at moisture contents between 43 and 49 %. The precize manner in which this hydration is effected may be important as certain barleys exhibit a water sensitivity in that submerged grain fails to germinate. Water uptake is initially passive but after *ca.* 20 hours becomes active. In the embryo the moisture content will rize to 60–65 %. During this germination, synthesis of depolymerizing enzymes takes place in both the aleurone and scutellum in response to secretion of plant hormones (gibberellins) by the embryo. Following diffusion through the endosperm, hydrolysis of cell wall material and starch and protein degradation will be initiated. These processes will continue at an accelerated rate during the mashing process. Germination is then terminated at the appropriate point and enzymic depolymerization activities temporarily halted by drying of the grain in kilns at moderately high (brewer's malt: 71–80 °C; distilling malts: 49–60 °C) temperatures. Management of the energy inputs into kilning is an important factor in the economics of the process. During kilning important non-enzymic or Maillard browning reactions occur largely between malt sugars and amino acids, but also including lipid breakdown products, generating many flavor compounds important to beverage and distillate character (Bathgate and Cook, 1989).

The practice of barley malting has changed markedly since the early 1970s so that the process is now highly mechanized, requiring capital-intensive plant and attention to the economics of the process.

Changes in Barley Cell-Wall Components During Malting

In the germinating barley, degradation of cell walls starts adjacent to the embryo and spreads in a broad band from the face of the scutellum and subsequently inwards from the aleurone. It is considered that the first stage in cell-wall breakdown is hydrolysis of the bonds between mixed β-glucans and proteins by an acidic carboxypeptidase β-glucan solubilase (Bamforth *et al.*, 1979; Wallace, 1988). The glucan is then hydrolyzed by *endo*-β-(1-3)(1-4)-glucanase activity which may either be endogenous or of microbial origins (Palmer, 1989). Although pentosanases or hemicellulases are also involved in cell-wall breakdown, Henry (1988) has concluded that β-glucan degradation is more obvious than breakdown of the pentosan component and various authors have reported that much cell wall and middle lamella material in malt remains even after extensive endosperm modification.

It is clear, however, that effective degradation of cell-wall carbohydrates will facilitate migra-

tion of proteolytic and amylolytic enzymes and thus allow efficient degradation of these polymers. Indeed incomplete cell-wall breakdown and endosperm modification has been shown to leave unextracted starch and protein in spent grain following mashing (Bathgate *et al.*, 1974).

Changes in Endosperm Proteins

Roughly two-thirds of barley storage proteins are located in the relatively inert endosperm tissue and one-third in the active aleurone layer. Protein is more abundant in the endosperm underlying the aleurone. It is clear that during hydrolysis of storage proteins into peptides which are subsequently converted into amino acids, the hordeins are preferentially degraded. In glutelins, albumins and globulins, little quantitative change is apparent during malting (MacLeod, 1979). Breakdown of the protein matrix, nevertheless, is important since this is a prerequisite for enzymic attack on the starch granules.

Protein breakdown in barley can be divided into three different phases. Initially, the protein bodies of the aleurone and scutellum are degraded by proteases and carboxypeptidases. This provides the amino acids necessary for synthesis of the enzymes that will effect endosperm modification. In the second phase, the storage proteins of the endosperm are hydrolyzed to generate further amino acids. In the third phase, proteins at the axis are depolymerized and breakdown products are taken up by the scutellum.

Proteolytic activities are important because during mashing amino acids are released into the extracting water (Table 1–2). These will act as nutrients for the fermenting yeast, producing biomass or serving as precursors for flavor compounds, and as buffering components for the pH of the wort. Residual proteins will emerge from the fermentation in beer production to contribute either to the foam in the head or alternatively haze formation.

Changes in Starch

Microscopic studies have shown that the breakdown of endosperm cell walls and protein matrix precedes degradation of starch granules. In barley the two types of starch granule, the larger type A and smaller type B, are degraded in different manners. The type B granules, associated with the matrix proteins, appear to be broken down by surface erosion. In the type A granules initial attack is restricted to a small number of sites. The starch depolymerizing enzymes appear to create channels with subsequent migration into the granule center. The enzymes then attack outwards from the channels into the crystalline starch.

Since germination in malting is carried out at ambient temperatures (in the UK typically 15–17 °C), starch is depolymerized by enzymes while extensively hydrogen bonded in the granule. In mashing when starch will have been previously gelatinized, depolymerization or saccharification is more rapid as the polymers will have been hydrated. Initially mobilization of starch takes place adjacent to the embryo near the ventrale crease. Attack proceeds to the distal edge of the kernel and then by an inward movement into the endosperm. Hydrolysis of intact starch granules is effected by α-amylases which release dextrins that may be branched, containing α-(1-6) bonds, or unbranched with only α-(1-4) bonds linking residues. The former may be hydrolyzed by limit-dextrinases, present both in the mature and germinating barley (Sissons *et al.*, 1993). β-Amylase, an *exo*-acting enzyme, hydrolyses product dextrins from the non-reducing end,

Table 1–2 Typical composition of a beer wort

Constituent	*Quantity (g/l)*
Fructose	2.1
Glucose	9.1
Sucrose	2.3
Maltose	52.4
Maltotriose	12.8
Non-fermentable carbohydrate	23.9
Total nitrogen (as nitrogen)	0.8
Total amino acid (as nitrogen)	0.30
Total amino acid	1.65
Total phenolic constituents	0.25
α-Isoacids	0.035
Calcium ions	0.065

generating maltose. This enzyme appears to be present in the mature endosperm and, in some varieties, it is largely in an inactive form bound to matrix protein, with the active catalytic form released by proteolytic activity in the germinating grain. In other varieties the majority of the enzyme is in a free (unbound) state and can be readily extracted from barley flour, by solubilization in water. Allison and Swanston (1974) noted differences in isozyme patterns between varieties with high or low proportions of free β-amylase. More recently these differences have been attributed to variation in β-amylase amino-acid sequences. Although there are five differences between the two patterns (Ma *et al.*, 2002), it is the substitution of cysteine for arginine at position 115 that promotes the formation of disulfide bonds and increases the proportion of bound β-amylase (Li *et al.*, 2002). This change also reduces pI and explains the differences between the two types observed by iso-electric focusing. Despite the synthesis and release of these enzymes, however, it has been calculated that, during malting, only 5-10 % of total endosperm starch is degraded, mainly at the embryonic end (Greenwood and Thompson, 1961).

Depolymerization Activities During Mashing

The Biochemistry of Mashing

Prior to mashing, malt is normally ground to produce a meal, described in whisky and beer production as the grist. This should not be ground too finely as this will slow subsequent filtrations. The coarse flour is mixed with water and the temperature increased either by heating or mixing with further hot water. During this hydration process the starch enzymes regain their depolymerizing activities. As the gelatinization temperatures are reached, starch granule structure is lost following the hydration and solubilization of the polymers. This dramatically increases the rate of enzymic depolymerization. The rate of heating during mashing is important and should be related to the degree of modification of the malt endosperm; particularly in undermodified malts there is a requirement for the relatively thermolabile β-glucanases and proteases to complete cell wall degradation prior to gelatinization or potential fermentables will be retained within the grain and lost to the process.

The result of mashing is the final mixture of carbohydrates, minerals or salts and potential nitrogen sources for production of yeast biomass. The components of malt can be supplemented by other cereals or their products, known collectively as adjuncts (Table 1–3). The resulting wort will be a solution of fermentable and unfermentable sugars, linear and branched dextrins, amino acids, peptides and proteins, lipids, organic acids and phosphates. The precise composition can be rather varied, related to barley cultivar and cereal adjunct, level of modification of malt, the enzymes present, both endogenous and in some cases exogenous, and their relative activities.

Depolymerization of Starch Polymers

The central enzymes in mashing are the α-amylases which are present in multiple forms, or isozymes. These have been divided into three groups (MacGregor and Ballance, 1980). Two of these appear to be the products of separate families of genes in the barley (Rogers, 1985); the third (group III) has been found to consist of the enzymes of the group II genes associated with a small polypeptide inhibitor, which also inhibits the activity of the protease subtilisin. The enzymes of the α-amylase group I are more active in degradation of large starch granules than enzymes of group II. The terminal glucose residue in dextrins produced by α-amylase activity is in the α-configuration. Activities of these enzymes have been reviewed by Berry and Paterson (1990).

The *exo*-acting β-amylases also yield the disaccharide maltose, with the free hydroxyl being in the β-configuration. β-Amylase activity ceases when an α-(1-6) branch point is reached. Size exclusion chromatography has suggested the presence of four different components, but these proteins have similar antigenic properties and appear to represent aggregates of a small number of polypeptides.

Although β-amylase is the main contributor to the total starch degrading activity of barley malt (Arends *et al.*, 1995), it is relatively heat-labile and, under certain circumstances, its activity during mashing may be reduced sufficiently for starch hydrolysis to become inadequate (MacGregor, 1990). However, Kihara *et al* (1998) noted that recently released Japanese malting barleys produced β-amylase with higher levels of thermostability than that found in European, Australian or North American varieties, increasing the fermentability of the wort. Eglinton *et al.* (1998) found elevated levels of β-amylase thermostability in an accession of the wild barley *Hordeum spontaneum*. These same authors also compared amino acid sequences of β-amylase from varieties with differing levels of thermostability and found three substitutions in one of the Japanese high thermostability types. One of these occurred in the C-terminal region of the enzyme that was removed when bound β-amylase was released during germination, so could not be responsible for the enhanced thermostability. A second substitution was later shown to be also present in a variety that did not show enhanced thermostability (Kaneko *et al.*, 2000). From these observations, it was concluded that the higher levels of β-amylase thermostability in Japanese barleys resulted from the substitution of serine for leucine at position 347.

Other enzymes active in the process of starch depolymerization are the limit dextrinases of which an active, free form, an inactive bound form and a third, latent form that is soluble, but inactive have been reported (Sissons *et al.*, 1993), (Walker *et al.*, 2001). The latent form appears to be a complex of limit dextrinase and barley protein inhibitors (Macri *et al.*, 1993), (MacGregor *et al.*, 1994). The release of glucose from the terminal non-reducing end of oligodextrins and maltose is achieved by a further

Table 1–3 Characteristics of adjuncts used in brewing

(a) Solid adjuncts

	Usage	*Moisture (%)*	*Extract (%) dry wt)*	*Protein (% dry wt)*	*Lipid (% dry wt)*	*Gelatinization temperature range (° C)*
Maize grits	Need cooking	12	90	9.5	0.9	62–74
Rice grits	Need cooking	12	92	7.5	0.6	61–78
Refined maize starch	Possibly cooked	11	103	0.5	0.05	62–74
Wheat flour	Possibly cooked	11	86	8.5	0.76	58–64
Torrified barley	No cooking	6	72	14.5	1.6	Pregelatinized
Flaked maize	No cooking	9	83	9.5	0.6	Pregelatinized

(b) Liquid adjuncts[a]

	Extract	*Glucose*	*Fructose*	*Sucrose*	*Maltose + maltotriose*	*Unfermentable sugars*
Solid sucrose	102	0	0	100	0	0
Invert sugars (glucose + fructose)	84	50	50	0	0	0
Maize (corn) syrup: high glucose	82	43	0	0	37	20
Maize (corn) syrup: high maltose	82	3	0	0	72	25

[a]Composition as % dry weight. Adapted from Hough (1985).

enzyme, α-glucosidase. The activity of these enzymes is much reduced at the elevated temperatures used for gelatinization of starches and, at mashing temperatures, α-amylases show the dominant depolymerizing activity, with stability being enhanced by the presence of calcium ions in wort. Thus in brewing, the minerals content of the mash water may be important in determining the fermentables present in the wort and the character of the final beer.

The limit dextrinase contained within malted barley extracts appears to be more heat stable than the purified enzyme and some activity is retained at the temperatures encountered during mashing (Stenholm and Home, 1999). However, significant levels of branched dextrins persist into the beer (Enevoldsen and Schmidt, 1973), suggesting that the degree of debranching activity during mashing may be limited. This may be due to the presence of starch degradation products that can inhibit limit dextrinase action (MacGregor *et al.*, 2002) in addition to the persistence of a significant portion of the barley protein inhibitors into the malt.

Cell-Wall Degradation

As both cell wall clucans and pentosans vary in their solubility in hot water, different fractions will dissolve as the temperature is increased to gelatinize starches. The activity of β-glucanases is much reduced at temperatures > 63 °C and mixed β-glucans are converted to gums that enhance wort viscosity and cause problems during drainage. The gelatinization and depolymerization of starch and solubilization of proteins at mashing temperatures will also result in further exposure of glucans and pentosans to hydration and solubilization. As the temperatures at which this will take place will be above those at which their respective depolymerizing enzymes are active, such cell wall carbohydrates appear as soluble polymers in the wort.

Genes coding for heat-stable β-glucanases occur in both fungi (Manonen *et al.*, 1993) and bacteria (Olsen *et al.*, 1991) and could, therefore, be targets for engineering into barley (McElroy and Jacobsen, 1995). However, despite considerable advances in developing genetic modification of barley (Jacobsen *et al.*, 2000), both technical problems and adverse public perceptions of genetically modified organisms currently remain to be overcome.

The heat-lability of barley (1-3, 1-4)–β-glucanase may result from unfolding initiating in the C-terminal loop, which appears to be an unstable region of the enzyme (Stewart *et al.*, 2001). These authors used site-directed mutagenesis of a cDNA encoding the enzyme to introduce eight amino-acid substitutions. Three that conferred increased thermostability were all located in the C-terminal loop. The largest increase occurred with replacement of the histidine at position 300 with proline, a mutation that should decrease the entropy of the unfolded state of the enzyme.

Protein and Nucleic Acid Solubilization and Breakdown

It has been calculated (Barrett and Kirsop, 1971) that most of the amino acids, or free α-amino nitrogen, extracted into the wort are released during malting rather than during mashing. However, protein breakdown continues during mashing as a two-stage process with an initial solubilization being followed by hydrolysis into peptides which decrease in size as proteolysis proceeds. In the second phase, peptides are converted into amino acids largely through the action of carboxypeptidases (Enari, 1972). It has been estimated that, in a typical malt wort, approximately 60 % of protein-derived material is present as amino acids, and 20 % as peptides. The residue is still high-molecular-weight polypeptides that may contribute to haze in beers.

Nucleic acids, present in malted barley, are solubilized and hydrolyzed to yield nucleotides which are rapidly converted to purine and pyrimidine nucleosides and finally free bases and sugars. This process may also contribute to the phosphorus essential for formation of yeast biomass.

Lipid Extraction During Mashing

Lipid extraction is influenced by mashing temperature, pH and thermo-mechanical proce-

dures used in the process. If high temperatures are used in mashing in combination with compression of the malt during the final filtration, elevated levels of lipid are extracted into the wort. This may have an influence upon the subsequent yeast synthesis of esters. It is, however, considered important that sufficient unsaturated fatty acids are present to produce appropriate levels of yeast growth during the fermentation.

Continued Activities During Distillery Fermentation

Degradation of Branched Dextrins

Branched dextrins have been detected in Scotch whisky distillers worts and, as they are not fermented by yeast, could represent a loss of potential alcohol yield (Bringhurst *et al.*, 2001). However unlike in brewing, distilling worts are not boiled prior to fermentation, so enzymes, including limit dextrinase, remain active under both laboratory and production conditions. The complexing of a portion of limit dextrinase to proteinaceous inhibitors in the mash appears to have beneficial effects. The complexed limit dextrinase survives inactivation during mashing (Walker *et al.*, 2001) and significant levels of free limit dextrinase become available well into fermentation, reducing final branched dextrin content and increasing alcohol yield (Bringhurst *et al.*, 2001). The mechanism for the release of free limit dextrinase is not fully understood, but may relate to changes in pH during fermentation.

Formation of Ethyl Carbamate

Traces of ethyl carbamate occur in many fermented foods and beverages and statutory limits may be imposed, due to the reported carcinogenic nature of the compound (Aylott *et al.*, 1987). In Scotch whisky, production of ethyl carbamate has been shown, primarily, to result from modification to a precursor present in barley malt (Cook *et al.*, 1990). The cyanogenic glycoside epi-heterodendrin (EPH) (Erb *et al.*, 1979) is produced in the acrospires of germinating barley grain and survives through kilning and mashing. During fermentation it is hydrolyzed by yeast β-glucosidase to isobuteraldehyde cyanohydrin (IBAC), which is unstable at temperatures above 50 °C, and dissociates during distillation to release hydrogen cyanide. In the presence of oxygen and copper, this, in turn, reacts with ethanol to form ethyl carbamate (Cook, 1990).

Levels of EPH production are influenced by the barley variety and by both the growing and malting environments (Cook *et al.*, 1990). In addition, the relationship between acrospire growth and EPH production appears to differ between varieties (Swanston, 1999). However, a number of varieties do not produce any EPH (Cook and Oliver, 1991) and this was thought to have resulted from a mutation, blocking the pathway, that had occurred in an Arabian land race used as a source of mildew resistance. Later work (Swanston *et al.*, 1999) confirmed the presence of a single genetic factor associated with EPH production on the same chromosome as several loci affecting disease resistance characteristics. Initial selection for non-producers of EPH was thus inadvertent, resulting from fairly loose genetic linkage, but these types are now preferred by many Scotch whisky distillers.

Multiple Parallel Fermentation

In conventional cereal fermentation, for example for beer and whisky production, the two essential stages of saccharification and alcoholic fermentation are carried out sequentially. The alternative approach is to use a non-malted saccharification, which runs simultaneously with the alcoholic fermentation, characteristic of saké and other oriental non-alcoholic fermented products. In this case the starch hydrolysis is achieved by *Aspergillus oryzae* (koji). The traditional process involves steeping in water and steaming of highly polished (removal of 25–50 % of the grain) rice, which is then seeded with spores of *A. oryzae* (Kondo, 1992). After 40–45 hours at 30–40 °C the rice is cooled to prevent further growth. Temperature and humidity control are crucial at this stage to control the fermentation. A yeast culture (moto) is prepared,

using either a spontaneous fermentation of airborne yeasts in a mixture of koji rice, steamed rice and water, or a defined strain of cultured yeast. Originally the fermentation was controlled by the growth of lactic acid bacteria, which prevented growth of spoilage organisms until they themselves were killed by the increasing ethanol concentration. Modern processes use an initial addition of lactic acid and higher temperatures to accelerate yeast growth. The final mash (moromi) is then mixed in three stages with further amounts of steamed rice, koji rice, and water being added to the moto over a period of 4 days. Fermentation then proceeds for 15–18 days to a final alcohol content of approximately 20 %, temperature control being critical for maintaining the balance of the fermentations. Distilled alcohol may then be added to halt the fermentation. The glucose concentration in the mash does not rise above 20 g l^{-1} during this process, allowing the relatively high final ethanol concentration. At the conclusion of fermentation, the saké is filtered, pasteurized, and may be aged for a time before further pasteurization and bottling at approximately 15 % ethanol. Modern variants of the process involve high temperature saccharification of rice prior to addition of yeast in making moto, and in the extreme a high temperature saccharification of the entire brew before adding moto, thus eliminating the system of mixing in three stages altogether.

Fruits as Raw Materials

Fruit Juices and Their Composition

Grapes and apples are the crops most widely grown for production of juices for fermented beverages. Processing of fruit is frequently largely mechanical, but, although this is convenient, losses in terms of flavor and in juice quality may be high through poor practice. Processing has a great influence on juice quality since pure apple juice, for example, when expressed from the fruit is essentially a colorless and odorless liquid. Within seconds a number of enzymic reactions take place, the juice turns brown and turbid and the characteristic odor of apple juice appears. Such juices also tend to sediment on storage (Lea, 1990). Grape juices have distinctly varied properties conferred by their composition (McLellan and Race, 1990): pigmentation through the presence of anthocyanins, their glucosides and condensation products (Hrazdina and Moskowitz, 1981); taste arises from the balances of organic acids, sugars and phenolic compounds (Ribéreau-Gayon, 1964); and aroma from a diverse mixture of secondary metabolites (Schreier *et al.*, 1976). This is typical of fruits. From the total amounts and balance of sugars and organic acids, sweetness and sourness in fruit juices can be estimated.

In both apples and grapes, mono- and disaccharides are the dominant carbohydrates. Lee *et al.* (1970) have estimated that the average grape contains per 100 g dry weight: 6.2 g glucose; 6.7 g fructose; 1.8 g sucrose, 1.9 g maltose and 1.6 g of sundry other mono- and oligosaccharides. In addition there are pectic substances which also appear in the juice. In apples, sugars constitute between 7 and 14 % of the fruit on a fresh weight basis, being almost entirely fructose, glucose and sucrose with traces of other sugars including xylose (Lea, 1990). Fructose always exceeds glucose by a 2- to 3-fold ratio. Sucrose is frequently present in similar amounts to glucose with contents of glucose falling as fruit matures. In apples low-molecular-weight sugars tend to increase during storage as starch is broken down. In the acidic conditions of most fruit juices, sucrose undergoes an inversion or hydrolysis into fructose and glucose.

In apples and pears, sugars synthesized in the leaves are transported to the fruit in the form of sorbitol, whereas in other fruits sucrose is the compound that is transported. In pears sorbitol contents may be as high as 20 g l^{-1} (Tanner and Duperrex, 1968) whereas in apples values between 4 and 12 g l^{-1} are typical. Starch may also be an important component in early season and under-ripe apples, forming up to 2 % of the fruit on the basis of fresh weight. Starch granules are found in a range of diameters between 1 and 16 μm, compartmentalized within storage vac-

uoles. If juices are heated above 60 °C during their production, apple and pear starches gelatinize, which may cause problems.

Organic acids are present in fruits at concentrations related to a number of factors including ripeness, genotype, season and climatic and agronomic variations. In apples, the major organic acid malic acid forms *ca.* 80 % of the total and is present at concentrations between 0.18 and 1.4 %, typically around 0.5 %. The balance of the acid content is largely quinic acid (0.04–0.46 %) with traces of citramalic and shikimic acids. In grapes, D-tartaric acid is predominant with significant quantities of malic acid. Many other acids are present in minor quantities in grapes (McLellan and Race, 1990). Grape juices are typically between pH 3 and 4; apple juices near to pH 3. Bertrand (1983) has concluded that for optimal wine aroma grapes should reach a good level of maturity so that pH of the must is relatively high.

The soluble protein content of many fruit juices is very low and in apples is in the range 10–250 ppm but generally < 100 ppm. In apple juices, 89 % of the soluble nitrogen compounds are free amino acids and of these 79 % is asparagine (Burroughs, 1984). In fresh apple juices the next most abundant nitrogen sources are glutamic and aspartic acids whereas tyrosine, tryptophan and cysteine were not detected. It is commonly believed that juices from dessert apples contain more amino acids than those from cider apples (Fisher, 1981) and that juices produced with apples from younger trees have higher contents than those from older trees. Amino acid contents of juices decrease with storage, largely as a result of the Maillard browning that takes place. This is in addition to the enzymatic browning reactions in which coupling of fruit phenols to polyphenols is promoted by the oxidative action of phenol oxidases.

Polyphenols of various structures are important to fruit-based fermented beverages such as ciders and wines, as a means of providing both mouthfeel and color. In the case of ciders, apple polyphenols such as chlorogenic acid and the epicatechin based oligomeric procyanidins play the most significant roles in both regards, as described in more detail by Lea (this book). In white wines, the oxidation of caftaric acid mediated by glutathione plays a major part in the formation of desirable golden-yellow tints while minimizing the advent of browning. In red wines, the extraction of anthocyanin pigments from grape skins during vinification is a matter of prime importance (Boulton, this book). Differentiation between certain red wines may be possible by means of the differing acylation patterns of the malvidin and peonidin glucosides which they contain (Etievant *et al.*, 1988). Grapeskins and seeds also contain high levels of oligomeric procyanidins whose contribution to the astringency of red wines forms an integral part of their character.

Volatile components confer distinctive flavors to fruits themselves, but these are not always carried through into their fermented counterparts in any significant way. Thus, most of the volatile aroma of cider derives from the action of yeast during fermentation rather than being derived directly from the volatiles of the fruit (Lea, this book). On the other hand, certain distinctive grape wine characters such as monoterpenes may be correlated with the sensory intensity of muscat flavors (Wagner *et al.* 1977) and the 'bell pepper' aroma of Cabernet Sauvignon appears to be inherent in the grape itself (Noble 1994). These topics are further explored by Cole and Noble (this book).

Fruit Pulping

Fruits have cell walls containing a greater range of polysaccharides than those present in cereals. A feature is the presence of the pectic substances, classified generally as pectins if > 75 % of monomers are esterified with methanol, or pectic acids (Figure 1–8). These polymers are often also referred to as galacturonans or rhamnogalacturonans on the basis of their relative contents of galacturonic acid and rhamnose. Arabinans, galactans and arabinogalactans are also referred to as pectic substances and the last may be found as linear and branched forms (Figure 1–8). The pectin component can form a significant component of fruits being 1.5–2.5 % of the wet weight of

apple pomaces. The cell wall in pears also contains approximately 16 % lignin, a polyphenol more commonly associated with woods.

Pectins are concentrated in the middle lamella between fruit cells (Figure 1–7). In intact tissue pectic substances are generally insoluble and are referred to as protopectins. Insolubility is a reflection of polymer molecular weight although divalent cations, such as Ca^{2+}, also contribute to retention of structure. The hemicellulose and cellulose content of fruit cell walls (the term pentosans being restricted to cereals) can also be rather varied. It has been estimated that pear cell walls contain 21.4 % glucose, 21 % xylose and 10 % arabinose (Jermyn and Isherwood, 1956), whereas those of apples contain *ca.* 76 % glucose, 1.2 % xylose and 6 % arabinose (Knee, 1973). A further complication is that a portion of the polysaccharides may be present as proteoglycan or polysaccharide-protein complexes.

This diversity and high content of cell wall carbohydrates can mean that processing of fruit requires treatments with exogenous enzymes to obtain adequate yields of juice of appropriate quality. A number of different enzymes are known to have roles in pectin solubilization and breakdown: polygalacturonases and pectin and pectate lyases being frequently described in the scientific literature although α-L-arabinofuranosidases and arabanases also have roles. Pectin methylesterases are also important in that these carboxylic acid esterases hydrolyze the ester bond releasing methanol into fruit musts. This may result in up to 2 % methanol which confers a sharp, burning character to distillates if the toxic compound is distilled over into the final beverage. Pectin and pectate lyases are *trans*-eliminases that are secreted by microorganisms whereas the hydrolases are endogenous to higher plant tissues.

Pulping of many fruits benefits from addition of exogenous pectinases of microbial origins. Enzyme treatments yield thin free-running juices with good pressing properties whereas with many fruits, notably blackcurrants, thermomechanical treatments alone generate semi-gelled masses. A further desirable side reaction is the presence of various glucosidases in industrial pectinases which enhance contents of flavor volatiles in musts through hydrolysis of precursor glycosides. There are significant benefits in the use of enzymes in breakage of grapes for white wine production since losses of varietal

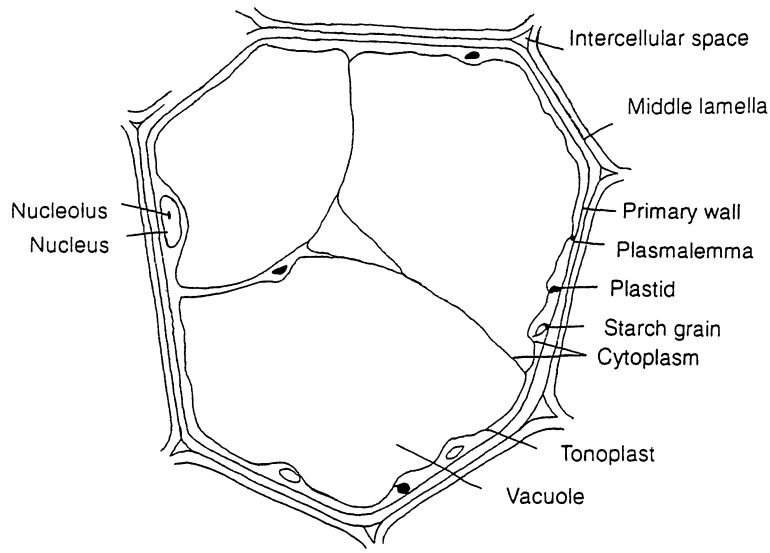


Figure 1–7 An idealized fruit cell structure (from Whitaker, 1984).

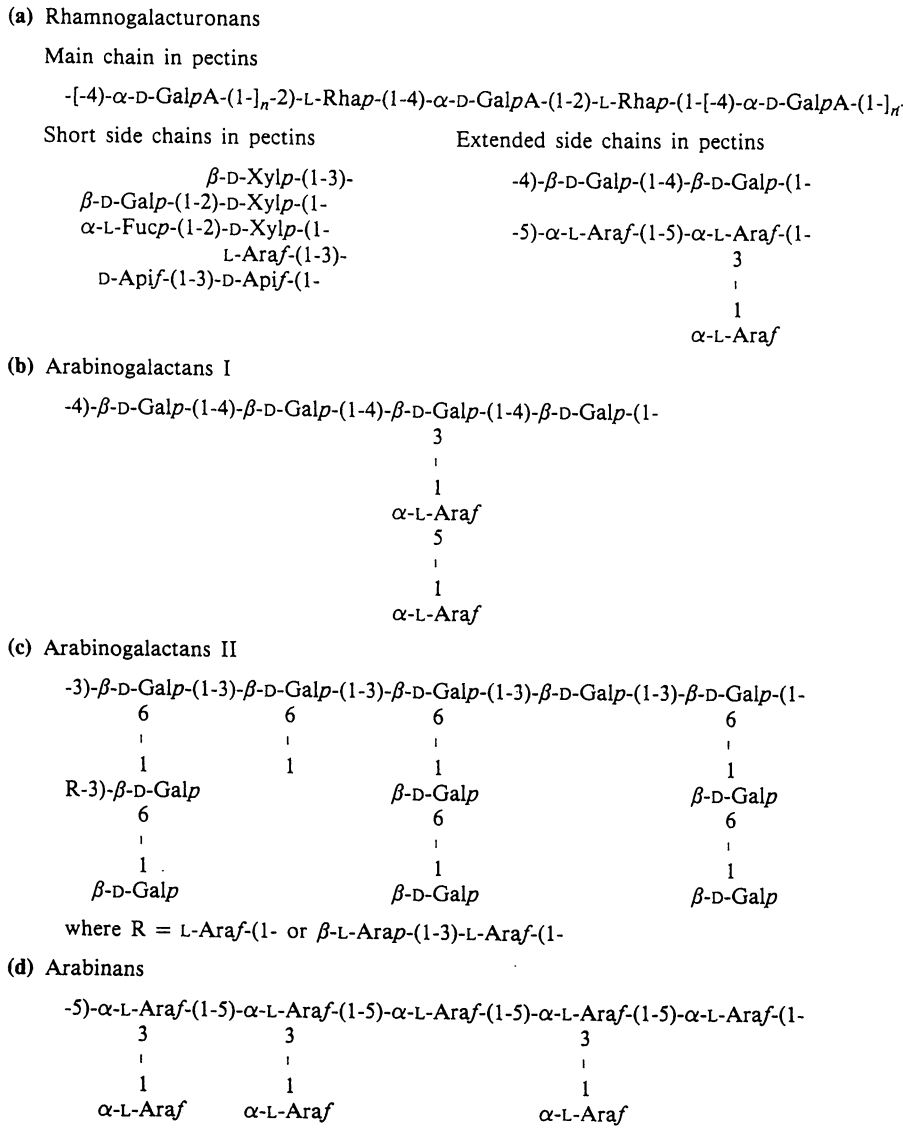


Figure 1–8 Hemicellulose arabinogalactan polymers in fruit (from Whitaker, 1984).

character can be reduced by minimization of thermal-processing treatments.

The presence of solids in grape musts may have an influence on the quality of the final wine. It has been shown by Bertrand (1983) that the presence of elevated levels of solids enhances the rates of CO_2 release during fermentation with a reduction in the final content of esters. Hydrolysis of esters in maturing wines is also favoured by low pH in the original must.

Implications of Processing Certain Fruits

Many fruits have specific problems or qualities that require care in processing.

Certain cultivars of fruit may have individual flavor characters requiring special processing pro-

cedures. In Williams pear distillates the varietal character arises from the presence of ethyl *trans*-2-*cis*-4-decadienoate. To maximize 'William pear' character, pears are processed when they are soft and nearly overripe. This requires extended storage and processing by gentle mashing in the presence of acid to prevent bacterial infections (Dürr and Tanner, 1983). Quinces also require special treatment as the exteriors of these hard fruits have hairs that contain volatile compounds which confer an off-flavor to distillates (Schobinger *et al.*, 1982). Excessive maceration of quinces should also be avoided as the pips have high contents of amygdalin. This is broken down to yield benzaldehyde, hydrogen cyanide and glucose. The legal upper limit of prussic acid in cherry distillates is 40 ppm; the lethal dose for humans is *ca.* 70 mg. The presence of this compound is thus a problem common to many distillates produced from stone fruits (Dürr and Tanner, 1983).

Kirsch character does not arize directly from volatiles present in the cherries used in its production. The fermented fruit mash is left for several weeks exposed to the atmosphere. During this period acetic acid formed by bacteria reacts with other compounds to yield large amounts of flavor-active esters that give the beverage its distinctive character. In raspberry distillates, where fruit is often extracted with ethanol rather than fermented because of the low sugar content of this fruit, contact between raspberry pulp and ethanol must be controlled. It is important to avoid excessive extraction of the seed oils which contain certain higher fatty acids: palmitic, linoleic and linolenic acids. These are subsequently esterified and although the presence of a limited amount of such esters enhances the perceived intensity of the raspberry odor, an excess generates off-flavors (Schöne and Sparrer, 1975).

Care is required in mashing of many fruit. Mashes, for example, from overripe plums have

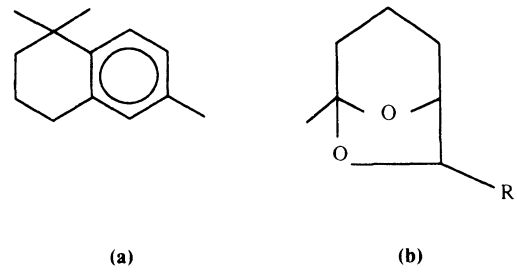


Figure 1–9 Structure of unusual compounds found in rums. (a) Ionene (b) brevicomin and analogues (R = Et, Pr, Bu) (from de Rijke and ter Heide, 1983).

a high pH and are consequently subject to bacterial infections and consequently taints from butyric acid or acrolein. If grape solid residues are left in contact with air for too long in production of Marc distillates, undesirable levels of methanol and acetaldehyde are formed (Dürr and Tanner, 1983). Interestingly, acetaldehyde is regarded as desirable and abundant in Puerto Rican, Jamaican and Martinique rums (Nykänen *et al.*, 1968). Moreover 2-ethyl-3-methyl butanoic acid, present in rums, probably arises from bacterial fermentations. Although sugar cane is a major crop for alcoholic beverage production, the properties of molasses as a raw material do not appear to be well understood. The presence of many terpenoids in Cognac can be explained by their presence in the grape, yet a large variety of these compounds are also found in rums (de Rijke and ter Heide, 1983). Ionene (Figure 1–9) is also present in rum distillates, the result of thermal degradation of vitamin A and the presence of brevicomin (Figure 1–9), a pheromone isolated previously only from the females of the western pine beetle *Dendroctonus brevicomis*, has also been reported in rums (de Rijke and ter Heide, 1983).

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2

Alcoholic Beverage Fermentations

D.R. Berry and J.C. Slaughter

YEAST

Most alcoholic beverage fermentations are carried out using strains of the yeast *Saccharomyces cerevisiae.* Although traditionally brewers distinguished between ale yeast *S. cerevisiae* and lager yeast *S. carlsbergensis,* or *S. uvarum* as it was later called, it is now recognized that these two species are completely interfertile and should be considered as one, namely *S. cerevisiae* (Gilliland, 1981). However, this is not to say that lager yeasts do not have some distinctive features, since the ability of the classical lager yeast to produce α-galactosidase and metabolize melibiose is well established. Similarly, strains defined as *S. diastaticus* have a well-established ability to metabolize low-molecular-weight dextrins, since they possess a glucoamylase gene. However, these strains are now considered to be strains of *S. cerevisiae* rather than distinct species.

The majority of distillers use commercial strains of *S. cerevisiae,* although the use of *Schizosaccharomyces pombe* has been reported for rum production. Saké yeast is also considered to be a strain of *S. cerevisiae.* The distinction between bottom-fermenting lager yeasts, which settle out at the end of the fermentation, and top-fermenting ale yeasts, which rise to the top of the fermentation and are skimmed off in the foam, is again no longer valid, since many ales are produced by yeasts that sediment out at the end of the fermentation, and many processes use centrifugation rather than the traditional techniques to remove yeast (Gilliland, 1981).

The situation in wine is much more complex; over 200 species of yeast have been isolated from wine fermentations from some 28 genera (Kunkee & Goswell, 1977). In spite of a great deal of research work by many laboratories, it is still not clear which are the most important yeasts in wine fermentation. Many modern wineries inoculate the fermentation with special strains of yeast, often *S. cerevisiae,* after having limited the growth of wild yeasts with sulfur dioxide. However, many wineries consider that diversity of yeast strains is essential for satisfactory flavor development. It does seem likely that strains of *S. cerevisiae* are important in all wine fermentations for the phase of rapid alcohol production.

Since the discovery of sexual breeding in yeast by Winge in 1935, classical genetic techniques have been used to obtain improved strains of brewing and distilling yeasts and for yeasts

for wine production. Since 1979, when there was the first demonstration of genetic engineering in yeast, these techniques have been used to introduce new characteristics into strains of *S. cerevisiae.* Some of these, such as the ability to ferment starch, production of ß-glucanases, and modification of flavor profile, could potentially be used in beverage fermentations. However, at the present time consumer resistance to the use of genetically engineered organisms has prevented the introduction of such strains into commercial processes.

Traditionally, inoculum was obtained for brewing and distilling processes by removing yeast from previous fermentations. In wine production, the presence of endogenous yeast on the skins of the grape was considered to be the source of the yeast inoculum. In each of these cases, the population of yeast obtained was mixed.

At the present time, most brewers continue to use this technique for inoculum production. Yeast is drawn off from a fermentation at the end of the growth phase, cleaned up by washing with acid, and stored before being inoculated into a new fermentation. This may be a mixed inoculum in some traditional breweries, but it is more commonly a special strain developed for the brand of beer being produced. This will have originated from a laboratory culture and may be replenished from this culture at intervals. Since yeast is destroyed during distillation processes, most distillers buy aerobically grown yeast to inoculate their fermentations.

The situation with wineries is more complex. Studies on yeast present on the surfaces of grapes have indicated that between 10^3 and 10^4 per ml colony-forming units can be found in must. These yeasts, which have arisen from the surface of grapes, contain several genera with *Kloekera* and *Hanseniaspora* spp. constituting 50–75 % of the yeast present, and *Candida, Kluyveromyces,* and *Hansenula* being frequently present.

However, the yeast *S. cerevisiae,* which is so dominant in wine fermentations, is either absent or present in very low concentrations on sound grapes and in fresh musts. It has become apparent that the indigenous population of *S. cerevisiae* develops in wineries as a result of growth on the surfaces of winery equipment in such a way that it permits each new batch of must to be inoculated with the same strain of yeast.

Special cultures of *S. cerevisiae* are now widely used in the wine industry and it is probable that commercial strains of other yeasts will become available to the industry. Quantitative studies have shown that although other species of yeast do grow during the first few days of the wine fermentation, *S. cerevisiae* becomes dominant and is probably responsible for most of the alcohol production. This has been attributed to the higher ethanol sensitivity of *non-Saccharomyces* yeasts. The growth of *non-Saccharomyces* yeast appears to be stronger in low-temperature fermentations (below 20 °C), which are more characteristic of red wine fermentations (Martini & Martini, 1990; Fleet & Heard, 1993). Many wineries buy commercially grown yeast to inoculate their fermentations; however, others are still dependent upon the natural flora of yeast or yeast that is present in the equipment and contaminates each new year's must as it is processed (Martini & Martini, 1990). Most of the rest of this chapter will be concerned with the physiology of *S. cerevisiae* in conditions of growth that are relevant to the production of alcoholic beverages.

PHYSIOLOGY OF YEAST GROWTH

Nutritional Requirements

In addition to requiring a carbon source and a nitrogen source, yeast also has a requirement for a range of metals such as magnesium, sodium, potassium, iron, zinc, copper, and manganese and other inorganic nutrients such as chloride, sulfur, and phosphate. It also has a requirement for vitamins, such as biotin, pantothenic acid, inositol, thiamin, pyridoxine, and nicotinic acid, if maximum rates of growth are to be achieved (Rose, 1977; Hough, 1985). Since the production of alcoholic beverages normally involves the use of complex substrates such as wort and

musts, the supply of these requirements is not normally a problem. If, however, complex substrates are diluted with adjuncts, then minerals and growth factors will be diluted and it may be necessary to add supplements. In strictly anaerobic conditions *S. cerevisiae* also has a requirement for sterols and unsaturated fatty acids (see below).

Carbohydrate Utilization

S. cerevisiae can grow on a limited range of carbohydrates. Brewing and distilling strains have the ability to take up and metabolize the monosaccharides glucose, mannose, fructose, and galactose; the disaccharide maltose; and the trisaccharide maltotriose. The disaccharides sucrose and melibiose can also be utilized, since the yeast cells have wall-bound enzymes, namely invertase and α-galactosidase, which hydrolyze these sugars externally so that their constituent hexoses can be assimilated. Some strains of *Saccharomyces,* the so-called *diastatic* strains, produce a glucoamylase that can attack α-(1-4)-linked dextrins of moderate molecular weight. Although the enzyme has been reported to act randomly on the dextrin chain and to be able to bypass α-(1-6) bonds, strains possessing this enzyme are not capable of completely metabolizing native starch (Stewart & Russell, 1987). The exact properties displayed by a yeast cell with regard to carbohydrate metabolism at any point depend on the composition of the medium, although the ability to take up and use glucose is never lost. A major control influence is the phenomenon known as catabolite or glucose repression. In the presence of readily metabolizable sugars, such as glucose, it was perceived some time ago that many cell functions such as mitochondrial respiration, synthesis of glucoamylase and invertase, and utilization of galactose, maltose, and maltotriose are repressed (Berry & Brown, 1987). As more information has been gathered, it has become clear that glucose also induces the synthesis of some enzymes and leads to the positive and negative covalent modification of existing enzymes. It both induces and activates plasma membrane ATPase, the enzyme responsible for creating a cross-membrane proton concentration gradient, thus stimulating uptake of amino acids and simple ions that are taken up via a proton symport system. It exerts control over the glycolytic pathway enzymes—particularly phosphofructokinase, fructose-6-phosphate phosphatase, and pyruvate kinase—through the RAS proteins, adenylate cyclase, and protein phosphorylation/dephosphorylation in such a way as to favor glycolysis over gluconeogenesis. The effect of this regulatory process is that sugars are assimilated from a complex mixture, such as a brewer's wort, in a defined sequence of glucose and fructose, followed by maltose and then maltotriose. In a brewery, the pitched yeast usually has a high invertase activity as it is collected from the end of a previous fermentation, essentially a glucose-free medium. Thus sucrose is usually utilized rapidly along with glucose. Yeast cropped from a glucose medium would not use sucrose until the glucose was largely consumed due to the repressive effect of glucose on invertase production.

Uptake of Glucose

Glucose can be seen as the preferred carbon and energy source of yeast but, despite much research effort, its mode of transport into the cell was not well understood until the late 1990s. Earlier work indicated that the process was by facilitated diffusion and the apparent K_m varied with the concentration of glucose in the medium. A few hexose transporters open to variable expression had been identified. Since publication of the complete yeast genome sequence in 1996 (Goffeau *et al.*), progress has been rapid. Genomic studies have allowed identification of a family of hexose transporters containing at least 20 proteins and, using this knowledge, mutants unable to grow on glucose were constructed for the first time. This required deletion of genes *HXT1* to *HXT7* and *GAL2*. Selected genes could then be inserted singly into these mutants and the characteristics of the transporter protein studied (Boles & Hollenberg, 1997; Nelissen *et al.*, 1997). Hxt1p and 3p are low-affinity trans-

porters, Hxt2p and 4p are moderately low, and Hxt6p and 7p and Gal2p have a high affinity. Snf3p and Rgt2p seem to be more involved with sensing the external concentration of glucose than with significant transport of the sugar. Chemostat studies have shown that transcription of *HXT1-HXT7* in complete strains correlated with the concentration of glucose in the medium whereas transcription of *GAL2* occurred only in galactose-limited conditions. The kinetics of glucose uptake under various conditions were consistent with the earlier data from single transporter strains (Diderich *et al.*, 1999). Active proteolytic degradation of the high-affinity glucose transporters Hxt6p and Hxt7p has been demonstrated when the concentration of glucose in the medium was substantially raised (Krampe *et al.*, 1998). It is now clear that glucose (hexose) transport in yeast is effected by a number of transport proteins whose concentration in the cell membrane is actively adjusted to the composition of the medium by control over gene transcription and protein turnover. Both the ubiquitin and vacuolar degradation processes seem to be involved in the latter process. The kinetic properties of glucose uptake as displayed by whole cells are therefore adjusted smoothly to the concentration of the sugar in the medium. A glucose transporter of some sort is always being expressed so that, while individual transporters cannot be said to be constitutive, this is true of the character (Ozcan & Johnston, 1999).

The exact nature of the glucose signal is still uncertain, although some possible mechanisms can be ruled out. Use of *hxt1* to *hxt7* null strains with single transporter genes reintroduced showed that glucose repression occurred regardless of the nature of the transporter. The strength of repression correlated best with the glucose consumption rate. However, glucose itself is not the signal, as the analogue, 2-deoxy-glucose, also stimulates repression. The analogue can be phosphorylated but not metabolized further, so the phosphorylation stage appears important rather than the downstream stages of the glycolytic pathway. This is supported by earlier observations that deletion of the *HXK2* gene, which is normally expressed constitutively, results in mutants that do not show glucose repression but grow normally on glucose. It may also be the case that yeast has more than one pathway for signaling the availability of glucose, one pathway that requires glucose uptake and involves Rgt2p and another pathway that is independent of uptake.

Glucose and the Uptake of Maltose

Although in most brewery and distillery worts glucose is not a major sugar, it exerts an undue influence because of the repression of maltose uptake and utilization. Maltose is the most important fermentable carbohydrate, followed by maltotriose, and the ability of the yeast to switch smoothly from use of glucose and fructose to maltose is very important in commercial fermentation. A slight pause in fermentation is referred to as a "maltose lag," while in more extreme situations fermentation ceases altogether; this is referred to as a "stuck fermentation." Supplementation of worts with glucose tends to exacerbate the problem because the switch in sugar source is pushed further back in the fermentation process when wort nutrients may become limiting and the cells therefore lack the competence to synthesize all the proteins necessary to make the change.

Uptake and utilization of maltose requires the expression of at least one of five highly homologous, but unlinked, sets of three genes. These are known as the *MAL* loci, *MAL1* to *MAL4* and *MAL6*. Gene 1 codes for the maltose transporter, gene 2 codes for maltase that hydrolyzes maltose to glucose inside the cell, and gene 3 encodes a regulatory protein. The uptake mechanism is proton symport; transcription of the genes is induced by maltose and repressed by glucose. More specifically, maltose appears to induce expression of *MALx3*, where *x* refers to the *MAL* locas. This process is blocked by *Mig1p* in the presence of glucose. *Malx3p* stimulates expression of *MAL1* and *MAL2* resulting in the uptake and utilization of maltose. Changes to the *MALx3* gene can lead to constitutive maltose utilization, whereas disruption of *MIG1* results in glucose-insensitive maltose metabolism.

Yeast strains able to utilize maltose in the presence of glucose are of commercial interest to both the brewing and baking industries. These strains should be immune from problems with the "maltose lag" and could possibly display a faster rate of metabolism by using both sugars simultaneously. At the moment, no generalizations seem possible and likely strains need to be evaluated under the appropriate production conditions to see if they can offer advantages without introducing new problems.

Industrial yeasts are able to use maltotriose completely, but this is usually the last of the fermentable sugars to be absorbed. An α-glucoside transporter encoded by the gene *AGT1* has been identified, and it is able to transport maltose, sucrose, trehalose, α-methylglucoside, and maltotriose. A recent survey of 30 brewing strains found that 29 contained *AGT1* and some of the strains contained *AGT1* homologues, but the role and control of the different genes in maltotriose uptake remain to be clarified.

Glucose and the Uptake of Sucrose

As mentioned above, sucrose is not taken up intact to any significant extent but is hydrolyzed outside the cell membrane to glucose and fructose by the enzyme invertase. This enzyme is located in the cell wall or the periplasmic space, and this results in very important differences in the fermentation characteristics of sucrose as compared to maltose on the industrial scale. Glucose represses synthesis of invertase just as it represses maltose metabolism in the early stages of wort fermentation. As the wort concentration of glucose declines, both sets of genes are released from repression and the enzyme systems for metabolism of both disaccharides are produced. When this yeast is repitched into fresh wort, which contains repressing concentrations of glucose, both sets of genes are turned off again and active degradation of the maltose transporter and maltase occurs within the cell so that maltose metabolism is lost rapidly after pitching. However, as invertase is located outside the plasma membrane, this enzyme is unaffected by the cellular control systems and the cells retain the ability to hydrolyze sucrose.

Utilization of Nitrogen Sources

S. cerevisiae can metabolize a number of nitrogen compounds. It can assimilate ammonia readily through active transport and can grow well with ammonium as the sole source of nitrogen except for a few vitamins such as biotin and nicotinamide. Urea is also a good source of nitrogen and is converted to ammonium within the cell. Nitrate and nitrite cannot be used. All α-amino acids can be taken up readily, as can small peptides. Proline can only be used under aerobic conditions, as its metabolism involves an oxidase-catalyzed step. The organic compounds vary greatly in their ability to sustain growth as single compounds, but mixtures of amino acids tend to support the best growth. Yeast has no extracellular protease activity and so cannot utilize large peptides or proteins. In industrial practice, as media tend to contain a wide range of amino acids and ammonium, and in some cases urea may also be added, availability of nitrogen is not usually a problem. In fact, the amount of assimilable nitrogen may be deliberately restricted to give just enough yeast growth. This tends to improve the efficiency of conversion of sugars to ethanol and CO_2 and makes the resultant alcoholic liquor less supportive of bacterial growth.

Differential uptake of nitrogen sources from mixtures has been known since the 1960s and appeared to result from control at the level of repression of gene transcription (Hough, 1985). Transport systems for ammonium, for amino acids in general, for small groups of amino acids, and for individual amino acids were all identified. Work using the yeast genome has confirmed these ideas and identified 24 amino acid permease homologues, of which 14 have a known function (Nelissen *et al.*, 1997). As this work progresses, significant functions other than transporting amino acids are becoming established. The genes *SSY1* and *PTR3* code for proteins that appear to have

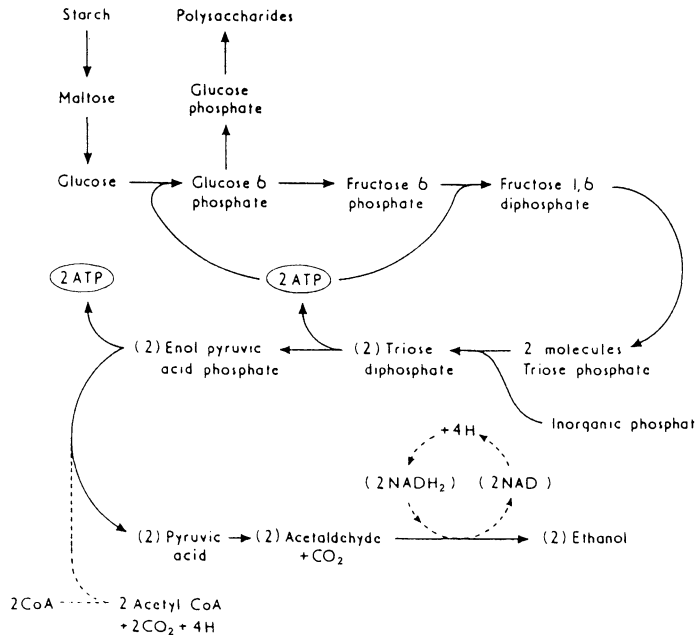


Figure 2–1a The Embden-Meyerhof-Parnas glycolytic pathway for glucose metabolism.

structures akin to the glucose uptake regulators Snf3p and Rtg2, and deletion experiments have shown a role for these genes in control of the transcription of the general amino acid permease gene. *MEP2*, the gene for the high-affinity ammonium transporter, appears to be essential for the transition to pseudohyphal growth that occurs in response to ammonium starvation; thus Mep2p may have a signaling function in addition to its role in taking up ammonium at low concentrations.

Ethanol Fermentation

During growth in anaerobic conditions such as those occurring in alcoholic beverage fermentations, all the ATP required for the growth is generated by the process of glycolysis (Figure 2–1a). Although some of the reactions of the TCA cycle may function to generate organic acids (Figure 2–1b) for cellular biosynthesis, the cell does not contain cytochromes and there is no generation of ATP by oxidative phosphorylation.

The factors controlling the rate of a biosynthetic pathway such as glycolysis are complex. However, it is evident that the supply of ADP in the cell is limited so that the overall rate of glycolysis will be limited by the rate that ATP is utilized by the cell in biosynthetic and other energy-requiring reactions and hence by the rate that ADP is regenerated. The production of pyruvate from glucose by glycolysis also generates two molecules of NADH. Again, the supply of NAD^+ in the cell is limited, so unless NAD^+ can be regenerated by NADH passing its hydrogen atoms to another molecule, the process of glycolysis will stop and growth will cease. The process of ethanol production is one in which NAD^+ is regenerated by the hydrogens of NADH being passed on to acetaldehyde, thus producing ethanol. The yeast *S. cerevisiae* is an unusual organism in that it can carry out this reaction very efficiently, giving a high yield of alcohol produced to glucose consumed. Clearly, some of the carbohydrate provided will be utilized to produce and maintain yeast cells. The overall reac-

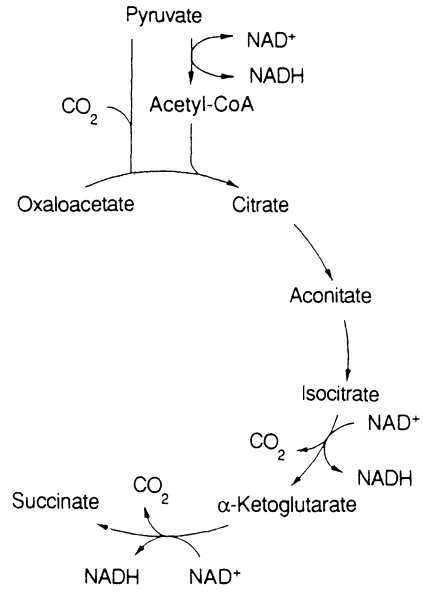


Figure 2–1b Tricarboxylic acid cycle activity in fermenting yeast.

tion for a brewery fermentation can be illustrated by the following equation:

Maltose + amino acid→yeast + ethanol +
100g 0.5g 5g 48.8g

carbon dioxide + 50 kCal (209 kJ) energy
46.8g

(dry weight)

Although in a well-run fermentation most of the sugar is converted into ethanol, it is normal for a small percentage to be converted into other byproducts. They include glycerol, organic acids such as succinate, and the flavor compounds that are produced in all ethanol fermentations. Glycerol is produced in the fermentation by the reduction of dihydroxyacetone phosphate, and this reaction regenerates NAD^+ when the supply of acetaldehyde is inadequate. A small amount of glycerol is produced in all fermentations, but this can be increased in certain conditions. Glycerol production can be stimulated by growth in conditions of high osmotic strength, growth in alkaline media, and growth in the presence of compounds that react with acetaldehyde, such as bisulfite. The production of glycerol can be considered beneficial in some fermentations—e.g., wine production—but is an undesirable process in the production of distilled beverages, since it represents a waste of substrate. In a well-run alcohol fermentation, glycerol has been reported to constitute 5.8 % of the total end product (minus carbon dioxide), succinate 0.9 %, yeast cell material (dry matter) 1.2 %, and ethanol 92.1 % (Korhola *et al.*, 1989).

In the early stages of alcoholic fermentations the rate of alcohol production increases exponentially in parallel with the increasing biomass. Once yeast growth ceases, however, the rate of production of ethanol proceeds linearly until the available carbon sources have been consumed. There is a reciprocal relationship between ethanol production and decreasing sugars and specific gravity. This period is often associated with the accumulation of storage carbohydrates such as glycogen in the yeast (Figure 2–2). These reserved carbohydrates may be converted into ethanol in a later stage of the fermentation when ethanol production proceeds at a very slow rate. Fermentations in which the inoculum was

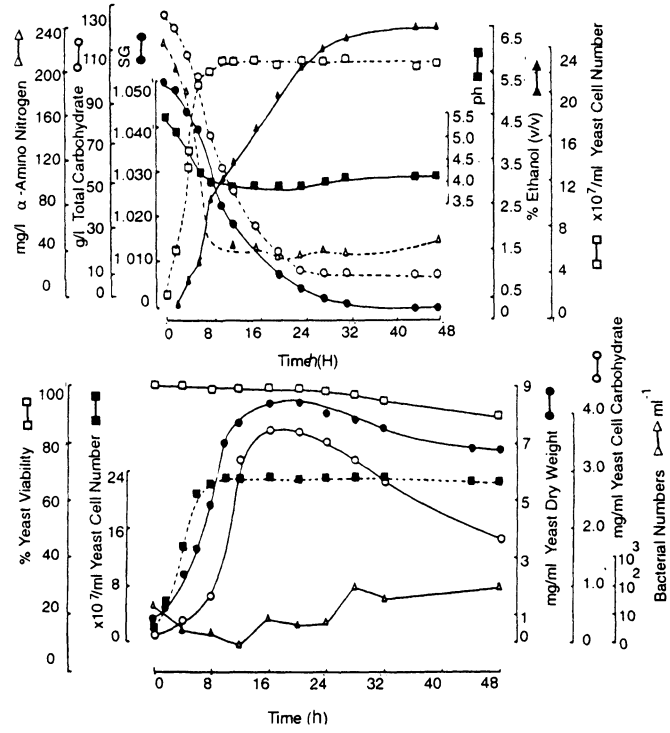


Figure 2–2 A small-scale malt whiskey fermentation showing changes in yeast cell number dry weight, carbohydrate content and viability, and bacterial numbers (from Ramsay & Berry, 1983).

obtained by recycling yeast from previous fermentations can frequently suffer from a problem known as a "sticking fermentation." This occurs when the yeast runs out of adequate supplies of unsaturated fatty acids and sterols to support growth. *S. cerevisiae* has a requirement for small quantities of these compounds but is unable to synthesize them in the absence of oxygen. This requirement can be satisfied either by the supply of unsaturated fatty acids and sterols in the growth medium (they are normally present in worts), or by the supply of adequate amounts of oxygen either during the growth of the yeast or during the fermentation itself. In brewing processes, this is normally supplied by a short period of aeration of the fermentation in a process known as "raising" the fermentation. In distilling, this is not normally a problem since the inoculum yeast is aerobically grown. In wine production, it has been suggested that medium chain-length fatty acids—e.g., decanoic acid and octanoic acid—produced by the yeast may have a key role in causing sticking fermentations.

In ideal conditions with an adequate supply of carbohydrate, some strains of *S. cerevisiae* have been shown to synthesize high concentrations of ethanol, in the order of 20 %. However, this does not mean that ethanol has no effect on the fermentation. Ethanol is inhibitory to yeast growth and metabolism and can slow down the rate of fermentation at much lower concentrations. It has also been demonstrated that the inhibitory effect of ethanol is markedly influenced by the growth conditions. Growth at high temperatures (above 32–33 °C) and at low pH values has a marked effect on the sensitivity of the yeast to ethanol. The effect of ethanol may also be influenced by the lipid content of the

medium as well as by the presence or absence of several salts—e.g., magnesium. The presence of other, higher alcohols in the fermentation may also contribute to alcohol toxicity, since higher alcohols are even more toxic than ethanol, their toxicity being related to their lipid solubility (Leao & van Uden, 1982).

The end of a fermentation may be associated with a period of yeast autolysis. This is true of any spirit fermentation in which the temperature rises above 33 °C (Berry, 1984). It is also a characteristic of processes in which yeast is left in contact with the beverage over a long maturation period, such as during champagne production. During autolysis, some components are degraded by endogenous enzymes releasing a range of products such as peptides, amino acids, fatty acids, nucleotides, and nucleosides, which can affect the essential properties of the beverage (Charpentier & Feuillat, 1993). As the scale of manufacture of alcoholic beverages has increased and the size of fermenters has become larger, attention has been paid to the effects of high concentrations of carbon dioxide, which can be generated at the bottom of the vessels. It has been demonstrated by several groups that carbon dioxide at 2–3 atmospheres can have an inhibitory effect on yeast growth and can also influence the rate of production of flavor compounds (Kruger *et al.*, 1992).

PRODUCTION OF FLAVOR COMPOUNDS

When yeast ferments sugars, ethanol is not the only product. Using modern methods of gas-liquid chromatography, it is possible to demonstrate that several hundred minor components are also produced. Some of these make an important contribution to the flavor of the product of the fermentation, be it a beer, wine, or wash for spirit production (MacDonald *et al.*, 1984; Berry & Watson, 1987). These can be divided into several categories based on their metabolic origins within the cell (Figure 2–3).

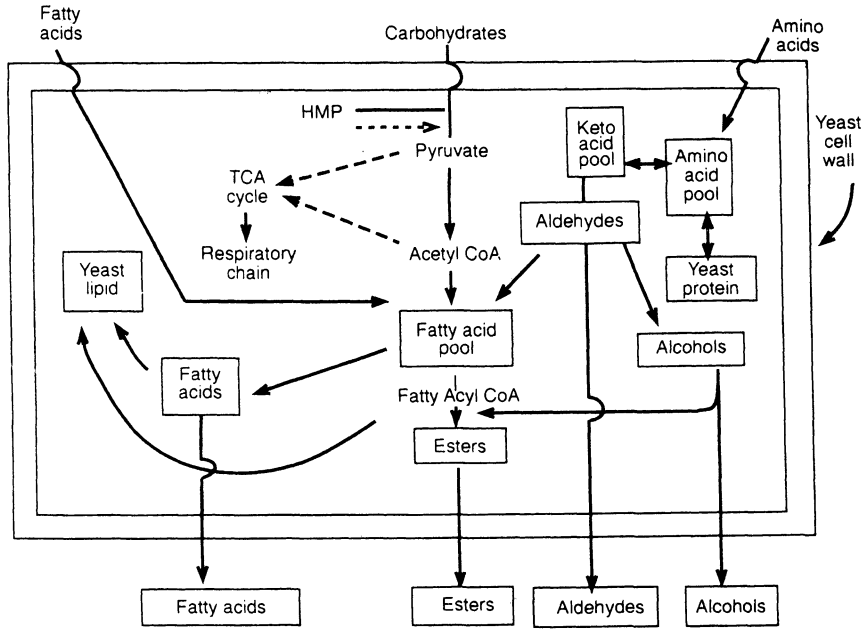


Figure 2–3 Basic routes by which yeasts form the major flavor groups during fermentation (Ramsay, 1982).

The most abundant of these are the higher alcohols whose production parallels that of ethanol. However, many compounds present in smaller amounts also have an important role to play in flavor development. Fatty acids such as acetate, medium-chain fatty acids such as caproate and caprylate, and long-chain fatty acids can contribute to the flavor directly or by being involved in the formation of esters. Carbonyl compounds such as acetaldehyde and diacetyl are present in even lower concentrations but have very low flavor thresholds so can play a key role in the flavor of the product. The yeast may also be involved in the production or modification of sulfur compounds, which can be of critical importance in the development of flavors and off-flavors in alcoholic beverages.

Higher Alcohols

Higher alcohols are produced from the carbon skeletons of amino acids. They may arise by the decarboxylation and deamination of amino acids present in the wort or by a biosynthetic route using the amino acid biosynthetic pathway of the yeast (Figure 2–4). Both these routes may occur in the same fermentation, with a switch from the degradative route to the biosynthetic route occurring when the amino acids in the wort have been metabolized. In general, conditions that favor a high growth rate tend to stimulate the level of higher alcohol production. These parameters include an elevated temperature, high inoculum levels, aeration of the medium, and replacement of sugars such as maltose by glucose. These general effects will increase the levels of all higher alcohols present in the medium; however, the levels of individual higher alcohols can be manipulated by altering the amount of the corresponding amino acid in the wort or must, or by genetically manipulating the organism so that producers may control the amount of a given amino acid or higher alcohol. This can be advantageous since certain amino acids induce a distinctive flavor; for example, phenylalanine stimulates phenyl ethanol production, a higher alcohol that gives a roselike aroma.

Organic Acids

The growth of all organisms including yeast requires a supply of organic acids for essential cell functions such as the production of cell membranes. Some organic acids that are excreted into the medium are derived from intermediary metabolic pathways—for example, acetate, malate, and succinate—but the major-

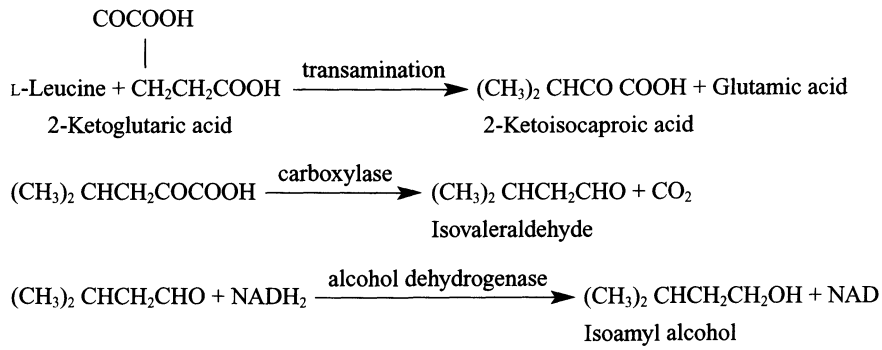


Figure 2–4 Mechanism by which isoamyl alcohol is produced from leucine.

ity of longer chain fatty acids are derived from the fatty acid biosynthetic pathway. However, fatty acids present in the medium can be assimilated and incorporated into the structure of the cell.

Acetate is the main organic acid excreted into the growth medium. It is produced by the oxidation of acetaldehyde by the removal of further hydrogens in a reaction that is the opposite of the normal reduction of acetaldehyde to ethanol. The rate of acetate production can be stimulated, for example, by the addition of alkali to the medium, which tends to stimulate the yeast to produce acetate and to adjust the medium to a more acceptable pH. During most yeast fermentations, the pH tends to decrease to around pH 3.5 to 4. Medium-chain fatty acids may be excreted into the medium and can give a goaty flavor to beverages; however, higher molecular weight fatty acids tend to be incorporated into the structures of the cell, usually in the form of phospholipids. Fatty acid production in general has been reported to be stimulated by higher levels of phosphorus, magnesium, and biotin (MacDonald *et al.*, 1984).

The metabolism of malic acid is of some importance in wine fermentations in which malic acid is converted into lactic acid by lactobacilli in a secondary fermentation known as the malo-lactic fermentation. This is more common in red wine fermentations than in the more acid white wine processes.

Esters

Esters constitute a major class of flavor compound in alcoholic beverages. They are produced by yeast during the fermentation in a reaction between alcohols, produced during the fermentation by the yeast, and acyl CoA molecules, which are key intermediates in the production of free organic acids. The amount of esters produced is dependent on the relative abundance of the corresponding alcohols and acyl CoAs produced by the yeast. Since acetyl CoA and ethanol are the most abundant acids and alcohols present in the fermentation, ethyl acetate is normally the most abundant ester. However, if good analytical techniques are used, almost every combination of acyl CoA and alcohol can be detected as esters in the fermentation product. The level of alcohol produced in fermentations is dependent on the nature of the product and can vary from less than 4 % in beers through 7 % for spirit production up to greater than 15 % in certain wines. The concentration of esters produced is normally increased as the level of alcohol rises and one of the unlooked-for consequences of high-gravity brewing has been an increase in ester production as a result of the higher levels of alcohol—and, indeed, higher alcohols—produced (MacDonald *et al.*, 1984).

Factors influencing the availability of organic acids and acyl CoAs are more complicated. Saturated fatty acids can be produced in all conditions, but unsaturated fatty acids and, in fact, key steroids such as ergosterol can be produced only when at least small quantities of air are available. Under normal growth conditions, most of the organic acids produced are then utilized for membrane biosynthesis. Under conditions of strict anaerobiosis, however, unsaturated fatty acids and sterols cannot be produced, so normal membrane formation is inhibited. In these conditions, organic acids become available for conversion into esters, which are excreted into the medium. Therefore, conditions that restrict growth, such as lack of aeration or nitrogen, should lead to an increase in ester formation. If the time course of ester formation is monitored throughout the fermentation, it is apparent that the majority of esters are produced in the later stages of the fermentation in contrast with the higher alcohols, which are produced largely during the growth phase and the period of rapid ethanol synthesis. Aeration of worts, such as occurs in the process of raising the fermentation, or the addition of unsaturated fatty acids and sterol by the addition of

trub leads to a stimulation of growth and a dramatic reduction in the level of ester production. Growth of yeast in a well-aerated system can totally suppress ester formation even in conditions that favor a high level of ethanol production (Berry & Watson, 1987).

Carbonyl Compounds

Carbonyl compounds, such as diacetyl, and aldehydes, e.g., acetaldehyde, play an important role in flavor development. Aldehydes tend to have very low flavor thresholds and also tend to have off-flavors. They are intermediates in higher-alcohol production, and conditions that favor higher-alcohol production also favor the formation of small quantities of aldehydes. These may be excreted but can be reabsorbed and reduced by yeast to the corresponding alcohol during the later stages of the fermentation. It has been reported that the level can be stimulated by the addition of sulfite and sulfur dioxide. This is most likely to occur in the production of grape products or other processes in which sulfur dioxide is used to control the growth of wild yeast or other microbial contaminants.

The most extensively studied carbonyl compound is diacetyl, which makes an important contribution to the flavor of lager-type beers, red wine, and some distilled products such as whisky and rum. Although its presence is considered essential for the correct flavor, excessive production can lead to off-flavors. Diacetyl is produced by the oxidative decarboxylation of hydroxy acids (Figure 2–5). However, the final concentration in the beverage is determined by the balance between the rate of formation and the rate of degradation. In the later stages of the fermentation, diacetyl can be metabolized by the yeast to acetoin and butane-2,3-dione. Diacetyl and pentone-2,3-dione synthesis can also be the result of contamination of the fermentation by certain strains of bacteria such as *Pediococcus* and *Lactobacillus*. Diketones, such as diacetyl, tend not to accumulate in conditions where there is sufficient active yeast present in the fermentation to break down the diketone, but although diketones may be produced more rapidly in vigorous fermentations, they are also metabolized more rapidly. However, in sticking fermentations there may not be sufficient yeast to break down diacetyl and it can, in such fermentations, frequently accumulate (MacDonald *et al.*, 1984). It has been well documented that lactobacilli influence spirit fermentations, including the whisky fermentation (Berry, 1984). Lactobacilli are also evident in rum production, and it is considered that their presence

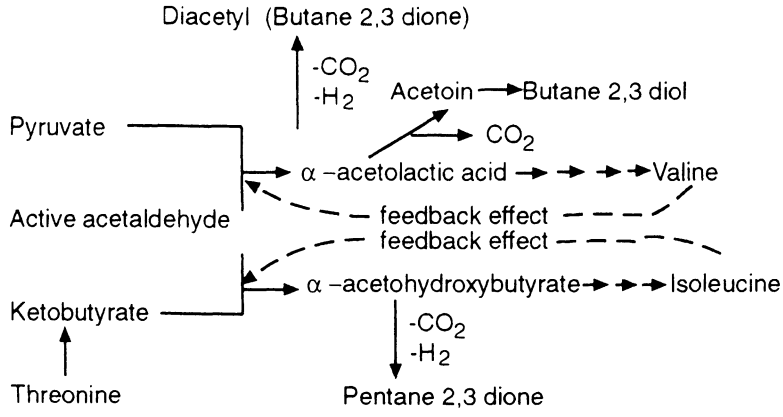


Figure 2–5 Reduction of the level of diacetyl in wort by reduction of α-acetolactic acid through a feedback mechanism.

influences the character of the final product (Fahrasmane & Ganou-Parfait, 1998). Yield of ethanol is also influenced, and Narendranath *et al.* (1997) have presented evidence that lactobacilli can cause up to 7.8 % loss of ethanol in the fermentation.

Malo-lactic Fermentation

The malo-lactate fermentation—the conversion of malate to lactate—occurs in the production of several beverages but has been mostly investigated in wine production, since the conversion of malate in the must to lactate is an important feature of wine production. It is carried out by malo-lactic bacteria and results in deacidification, as indicated by an increase in pH and a decrease in titrable acidity. The reaction is carried out by the so-called malo-lactic enzyme, which decarboxylates L-malate to L-lactate and carbon dioxide. This is lost to the system in the form of bubbles. The reaction involves Mn and NAD+, but the latter does not decrease in amount so does not appear to be directly involved in the reaction as a substrate.

The malo-lactic fermentation can be carried out by a range of lactic acid bacteria of the genera *Lactobacillus*, *Pediococcus,* and *Leuconostoc,* which have been isolated from wines. Which species predominates depends upon several physiological parameters, but pH and ethanol concentration are particularly important. *Oenococcus oenis* (formerly *Leuconostoc oenos*), the name given to all *Leuconostoc* strains isolated from wines, is especially tolerant of low pH values, so it tends to predominate in acid wines below pH 3.5. Since many bacteria can have a deleterious effect on wine flavor, modern wine production processes involve the addition of high concentrations of starter cultures of selected lactobacilli, which ensures that the correct fermentation occurs (Henick-Kling, 1993). Lactobacilli in wine are not only able to metabolize malate to lactate but can also metabolize citrate present in wine into pyruvate, lactate, ethanol, acetate, and diacetyl (Nielsen & Richelieu, 1999). The production of diacetyl is particularly important, since it can directly influence flavor. The amount of diacetyl produced is influenced by the quantity of citrate, and the redox potential and oxygen concentration in the wine. The amount present is also influenced by the concentration of free SO_2.

Since a high level of titrable acidity gives rise to sourness, a reduction in it will lead to a reduction in the tartness of the wine. However, the concomitant increase in pH can lead to a reduction in the stability of the wine and a potential increase in microbial contamination. Strains of *Leuconostoc oenos* are widely used as starter cultures, not just because of their tolerance to pH and ethanol concentration but also because of the contribution that they make to mouth feel and their influence on flavor. The influence of lactobacilli on wine development is augmented in some wines such as Chardonnays by using a *sur lees* treatment during their production. Several other strategies have been investigated for the control of the malo-lactate fermentation, such as the use of immobilized enzymes (Valihout & Formisyn, 1997) and genetically engineered yeast (Bony *et al.*, 1997).

The malo-lactic fermentation is also important in the production of cider, and it has been reported that temperature is an important parameter in controlling such a fermentation in cider production (Herrero *et al.*, 1999). Although the rate of malate metabolism increased at higher temperatures—e.g., 27 °C—22 °C was preferred, since at this temperature less acetic acid is produced.

Sulfur Compounds

Although some 50 volatile sulfur compounds have been identified in alcoholic beverages, the majority of these are derived directly from raw materials. However, some are derived by the sulfur metabolism of the yeast. Hydrogen sulfide can be produced during the breakdown of methionine and cysteine released during yeast autolysis or protein turnover. It can also be generated from inorganic sulfur if this is present in

the medium. Yeast can also produce dimethyl sulfide (DMS) from such precursors as *S*-methyl-methionine and D-dimethyl-Sulfoxide if these are present in the medium. It is not considered that the yeast is an important source of DMS, which is more likely to be present in high quantities in raw materials such as malted barley. However, yeast strain is considered to be an important factor influencing the production of hydrogen sulfide, since the amount formed under defined conditions appears to be characteristic for a particular strain. Normally, hydrogen sulfide produced during the fermentation is purged by the effect of the rapid evolution of carbon dioxide; in less vigorous fermentations and in extended periods at the end of fermentations when autolysis may be occurring, sulfury odors can develop.

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3

Beers: Recent Technological Innovations in Brewing

D. Iserentant

INTRODUCTION

The brewing industry is a traditional one: many brewers are using a technology that remained basically unchanged over a period of 100 years. New technological breakthroughs are seldom directly applied to the brewing process; most of the brewers are afraid that the change would harm either the quality or the image of their beer. In recent years, the situation has been changing: fusions and takeovers have created big brewing groups, and increasing competition in a shrinking beer market has forced the brewer to be more cost effective than before. Technological innovations are used now to increase productivity, to save energy, or to create new products.

There will probably always be a market for the small, traditional brewer. The larger brewing groups, however, need to closely follow technological changes. Successful incorporation of the technological innovations in the brewing process will largely determine the strength and the competitiveness of the brewery in the future.

THE TRADITIONAL BREWING PROCESS

Raw Materials

Malt. The brewing process normally starts from a starch-containing crop, from which, during the brewing process, the starch is saccharified by the endogenous enzymatic activity of the grain. The normal starch source is malted barley. The barley used by the brewers differs from feed barley: normally, the brewer prefers a two-row spring barley with big kernels. Although the barley has some technical advantages—it is easy to malt and the husks are an essential tool during the lauter tun filtration—the use of barley is historically determined rather than a technical or economical necessity. In many cases, a smaller or larger part of the malt is replaced by adjuncts—i.e., other starch sources (normally rice or corn) or even sugar syrups.

Barley is malted to induce the enzymatic activity of the kernel and to obtain a first modification of the grain (starch conversion into fermentable sugars by amylases, but also cell wall

polysaccharides degradation by the action of ß-glucanases and xylanases). The malting process can be considered as an induction of the germination of the grain and is followed by a heat treatment—the kilning—to stop the germination process at an early stage. By choosing the conditions of the malting and kilning processes, different kinds of malts can be produced. One important factor is the degree of malt modification, i.e., the degree of starch and ß-glucan degradation obtained during malting. Another important factor is the color of the malt. The color is mainly determined by the kilning temperature; pale malts, kilned at relatively low temperature (about 80 °C as highest temperature) are normally used for lager beer production. Darker malts, kilned at higher temperatures (e.g., Munich, caramel, chocolate malt) are used for the production of special beers. These special malts are important for both the flavor and the color of the special beers.

In some regional ales, a large part of the malted barley is replaced by wheat, or sometimes rye or oat. The high amount of unmalted cereal results in a hazy beer that is not filtered but consumed as such (so-called white beers).

Water. Water makes about 90 % of the finished beer; it should not be neglected as a quality-determining factor during the brewing process. The brewing water has to meet the same high standards as drinking water.

The mineral content of the brewing water is very important: some minerals (magnesium, zinc) are important for a fast and regular fermentation. Moreover, salts may determine, among other factors, the typical character of some special beers. A well-known example is the high sulfate character in the water of Burton-type ale.

Whereas brewers at one time were dependent upon the water quality of the local source, it is possible nowadays to adapt the water quality and the mineral content of the water to the needs of the process.

Hops. The use of hops in brewing dates back to the Middle Ages. At that time, hops were replacing the special spices that were used before. Today, brewers still use hop for its bittering and aromatic properties. Hop, however, also has antiseptic properties (Simpson & Hammond, 1991; Smith & Smith, 1993).

Hops are normally added during the kettle boil: during the boiling process, the α-acids of the hop are isomerized, which is important to obtain the right bitterness in the final beer. Sometimes, fresh hops are added during fermentation of the finished beer to avoid the loss of volatile acids during boiling and to retain the aromatic qualities of hop in the beer. This procedure is called "dry hopping."

Hops can be added as hop cones or as milled hop, but, more and more, the milled hop powder is pressed into pellets and used as such. Hop pellets have a higher bulk density than baled hops and are easier to store and to handle. However, the hop powder is rapidly accessible to oxidation, and the pellets should be packed properly to avoid deterioration.

The hop α-acids and flavors can also be extracted by a solvent (low-molecular-weight alcohols, ketones, hexane), or by liquid CO_2. The solubilization and isomerization of the hop α-acids occurs more rapidly in extracts than with whole hop cones. A comparison of the use of different hop extracts has recently been published by Forster *et al.* (1996).

Yeast. Yeast is one of the most important flavor-determining elements of the beer. Brewer's yeast belongs to the genus *Saccharomyces* and is now normally classified as *Saccharomyces cerevisiae* (Yarrow, 1984). However, brewer's strains are more complex than the taxonomical type strain: brewer's yeast is normally polyploid or aneuploid and sporulates rarely. Brewers make a distinction between top-fermenting yeast (formerly *S. cerevisiae*) and bottom-fermenting yeast (formerly *S. carlsbergensis* and *S. uvarum*). Top-fermenting yeast, used for ales, ferments at relatively high temperatures (18–25 °C), and the yeast crops normally float at the top of the fermented wort at the end of the fermentation. The bottom yeast is used for lagers. The fermentation temperature is lower (8–12 °C), and the yeast flocculates to the bottom of the tank at the end of the fermentation. Bottom yeast differs biochemi-

cally from top yeast by its use of melibiose and raffinose. Recently, other phenotypical differences—such as the pattern of mixed carbohydrate fermentation, the carbohydrate transport, and the sensitivity to cations—have been described (Crumplen *et al.*, 1993). Pedersen (1983, 1985, 1986a, 1986b) compared extensively the genomic organization of several lager and ale strains. Whereas there is a large variability among the top-fermenting strains, all the lager strains seem to be related and may originate from one single strain, probably produced by hybridization of a top-fermenting *S. cerevisiae* strain and a bottom-fermenting *S. monacensis* strain (Pedersen, 1986b).

Some special beer types are produced by mixed cultures that may contain other yeast genera such as *Brettanomyces* (in the case of Gueuze) or even lactic acid bacteria (for Gueuze, Berliner Weisse, acid ales of Flanders) (Martens *et al.*, 1997).

Wort Production

Mashing. The mashing procedure is intended to produce and extract fermentable sugar from malt. Therefore, the malt should be milled to optimize the transformations and to improve the solution of the extractable material. However, the husk of the malt should remain intact to serve as a natural filter during lauter tun or mash filtration. This can be achieved in a roll mill, where the grist fractions are separately treated depending upon their size. Sometimes, the grains are steam conditioned to enhance the moisture content of the husk (wet milling). This treatment renders the husk less liable to fragmentation and allows a finer milling of the other fractions.

The malt flour is mixed with water and heated to allow enzymatic degradation of high-molecular-weight compounds, such as polysaccharides and proteins. Single-temperature infusion mashing is probably the simplest system: the mash is kept at a temperature of approximately 65 °C for a period of time. This mashing procedure is carried out in a single vessel, which is used in most cases for lautering (filtration to remove the insoluble fraction), too. The infusion mash is often used in the United Kingdom for the production of ale wort. This system, however, can be used only with well-modified malts; for less-modified malts a temperature profile is applied during mashing. The temperature is raised and kept for a certain time period at the optimal temperature for the specific enzymatic conversions that the brewer wants to obtain. The temperature steps are normally 50 °C (protein rest) as optimal temperature for protease, 62 °C (maltose rest) to allow the action of β-amylase, and 72 °C (saccharification rest) as optimal temperature for α-amylase. α-Amylase is an endo-enzyme that cuts the starch into rather big fragments, whereas β-amylase produces maltose. Because β-amylase works at a lower temperature than α-amylase, it is impossible to obtain a complete conversion of starch into maltose by the conventional mashing process: some larger polysaccharides (dextrines) remain in the wort. The temperature steps should be controlled carefully to obtain sufficient saccharification.

The temperature-profile mashing procedure can be carried out by heating the mash in one stirred vessel, or by the so-called decoction procedure. During the latter process, a part of the mash is pumped into a second vessel, heated to boiling temperature, and re-added to the main mash. By mixing the two parts, the temperature of the main mash is raised. The decoction procedure is especially useful when adjuncts are used; it allows a separate treatment of the unmalted adjuncts that generally have a higher starch gelatinization temperature than malt.

Filtration. After the mash, the liquid (wort) is separated from the spent grain. This is usually done with a lauter tun or with a filter press. The lauter tun is a vessel with a flat perforated bottom. At the beginning of the filtration, the husks settle rapidly to build up a natural filter on the bottom of the vessel after a few minutes. During this period, the wort is recirculated; once the filter is formed, the wort is filtered with the help of the husks. A lauter tun gives wort of an excellent quality—i.e., a clear wort that is low in lipid content—but the filtration is rather time consuming

and the removal of the spent grains may be difficult.

The strainmaster can be considered a special form of lauter tun, but the vessel contains slotted pipes of triangular cross-section instead of a perforated bottom. For the same floor space, the filtration area is bigger than that of the lauter tun. The runoff is rapid and the wort is of good quality, but, because of the method of discharge, the spent grains are very wet.

The mash filter consists of several hollow frames and plates, separated by filter cloths. Wort is pumped in the frames and, similar to the lauter tun, a filter is formed by the husks. This form of filtration is more rapid and easier to automatize than the lauter tun filtration, but the filter wort contains more lipids and is not as clear as that from the lauter tun.

After the main filtration, the filter is washed to remove as much extractable sugar as possible from the spent grains (sparging). This washing improves the extract yield of the filtration, but results in a dilution of the wort, which has to be corrected by evaporation during boiling.

Wort boiling. The main reasons for wort boiling are to inactivate the enzymes (amylases, proteases, β-glucanases) and sterilize the medium for the subsequent fermentation. However, boiling of the wort has several secondary effects that are nearly as important. During the 1.5- to 2-hour boiling period, proteins coagulate (hot break), which plays an important role in the physical stabilization of the beer: insufficient protein coagulation would cause haze formation during storage of the finished beer. Hop acids are isomerized and new flavors are formed by Maillard reactions. The same Maillard reactions are darkening the color of the wort, which is an important quality factor for pale beers. Unwanted color formation may limit the total boiling time.

During boiling, some unwanted flavor compounds—such as dimethylsulfide, which originates from the malt—are evaporated. Moreover, the wort is concentrated at an evaporation rate of about 8 % per hour.

The boiling is traditionally executed in a open-top vessel at atmospheric pressure, and heat is provided by a heat jacket or by an internal heat exchanger.

Wort Fermentation and Maturation

Fermentation. After the wort boiling, the hot break is removed (by a whirlpool, a centrifuge, or a hot settling tank) and the wort is cooled, oxygenated, and pitched with yeast. In most breweries, pure yeast cultures are used. Usually the yeast used for pitching is recuperated from a previous fermentation. However, most brewers reuse the yeast only a limited number of times, to avoid yeast contamination and degeneration of the strain. In that case, at regular time intervals, a new yeast culture is propagated, starting at lab scale from pure stock culture, to replace the pitching yeast when this limit is reached.

The fermentation temperature and the duration of the fermentation depends upon the type of beer—for a lager beer, it takes about seven days with a wort of 12 °Plato (12 g sugar per 100 g solution; this is considered a "normal gravity" wort). For ales, which are fermented at higher temperature, the fermentation time is normally shorter.

During fermentation, the sugar (mainly maltose and smaller amounts of glucose, sucrose, fructose, and maltotriose) is converted into alcohol. There is an important flavor production during this period, too: the esters (ethylacetate, isoamylacetate, etc.) and higher alcohols (propanol, butanol, isoamylalcohol, etc.) will determine to a great extent the character of the final beer.

For lager beer, the main fermentation is followed by a maturation period of several weeks. Most ales do not have such a long maturation period and are filtered shortly after fermentation. Indeed, several special post-fermentation treatments such as refermentation in bottle or aging in wooden casks are known for special regional beers. In these cases, an adaptation of the normal maturation and filtration process is required.

Formerly, the fermentation was carried out in open vessels, but nowadays most brewers are using closed cylindroconical vessels. These tanks have a conical bottom that allows an easy

harvest of the yeast that flocculates to the bottom of the tank during lager fermentation.

A review of beer-fermenter design and a description of alternative forms of fermenters is given by Maule (1986).

Maturation. After the main fermentation, the flocculated yeast is removed and the beer is cooled down for maturation. During maturation, the remaining sugar is fermented and the beer becomes saturated with the CO_2 produced. The taste of the beer becomes refined, the most important transformation being the reduction of the butter-like flavor diacetyl. Diacetyl is a byproduct of the isoleucine/valine synthesis and is formed by decarboxylation of α-acetolactate (Figure 3–1). Yeast reduces diacetyl to the flavor-neutral compounds acetoin and butanediol. During the maturation, there is also a further flocculation, leading to an improved clarification of the beer. The classical maturation takes several weeks or even months. It is carried out in a closed horizontal vessel or, more often now, in a cylindroconical vessel similar to that used for the main fermentation. After maturation, the beer can be filtered to remove the remaining yeast and is then ready for bottling and consumption.

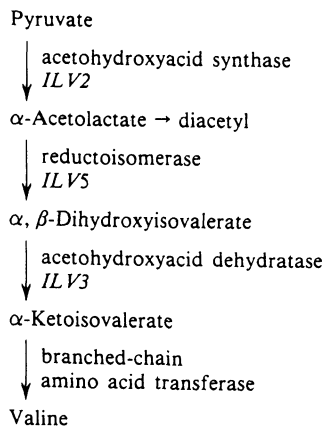


Figure 3–1 Diacetyl production by yeast. Diacetyl is a byproduct of valine biosynthesis. Intermediates, enzymes, and genes of the pathway are indicated. α-Acetolactate is secreted by the cell and decarboxylated in the medium to give diacetyl. Yeast cells can take up diacetyl and reduce it to acetoin and butanediol.

The products. Giving here a complete overview of all beer types is impossible: beer exists in a large diversity of color, from colorless to nearly black; in a large diversity of alcohol content, from alcohol free to products that have an alcohol content up to 12 % volume; and in a large diversity of taste, from rather neutral to bitter, acidic, or even spicy. An overview of this diversity can be found in special beer guides. However, most of the special beers have a regional character, and the majority of beer sold all over the world is of the Pilsener type. Pilsener is a pale beer (about 7 EBC color), with an original gravity between 12 °Plato and 13 °Plato, an alcohol percentage of about 5 % volume, and a bitterness that is regionally determined, from neutral in the United States to strongly bitter for some German beers (EBC bitter units varying between about 16 and 30).

NEW TECHNOLOGICAL EVOLUTIONS

Raw Materials

New barley varieties. A review of the progress in barley breeding is out of the scope of this chapter. Reviews on this subject have been published by Pitz (1990), P. Hayes (1991), and Palmer (1992). A comparison of recently bred barley varieties has been published by Schildbach (1998).

It may be expected that genetic modification of barley will become an important tool in barley improvement in the future (Lörz *et al.*, 1995).

Improvement in malting technology. During recent years, maltsters have become aware that malting is not only a plant physiological process, but that microorganisms play a determining role in malt quality. This insight has led to the use of starter cultures in malting. Boivin & Malanda (1993) reported on the use of the bacterium *Lactobacillus plantarum* and of the yeast *Geotrichum candidum.* Both strains were able to reduce the production of the mycotoxin zearalenone by the fungus *Fusarium*, but the yeast was

more efficient in that respect. Haikara and coworkers (Haikara *et al.*, 1993, Haikara & Laitila, 1995) applied lactic acid bacteria as starter culture during steeping in laboratory and pilot plant maltings. The *Lactobacillus plantarum* strain used proved to be effective in limiting the *Fusarium* contamination and in reducing the deoxynivalenol and zearaleone formation during malting (Laitila *et al.*, 1997). Moreover, even severe problems in mash filterability, caused by barley containing a high number of split kernels, were readily alleviated by treating the grain during steeping with a starter culture (Laitila *et al.*, 1999).

Physical pre-treatment of adjuncts. Several researchers have proposed the use of pregelatinized adjuncts, so that the gelatinization during mashing could be avoided, allowing a simpler mashing procedure. A pregelatinized adjunct would be a rather cheap replacement for malt and could be used in relatively large amounts (20–30 %).

Gelatinization of the adjunct can be achieved by micronization or by extrusion. *Micronization* is a process in which cereal grains are subjected to infrared radiation generated from burner-heated ceramics. Micronized wheat has been successfully used in brewing. However, the use of micronized wheat can lead to filtration problems and loss of brewhouse performance (Brookes & Philliskirk, 1987; South, 1992). *Extrusion* is a technique in which cereals are compressed at relatively high temperature. Although the technique was initially developed for the plastics industry, many applications are known in the food industry, especially for the production of snack foods. The potential usefulness of extrusion to brewing has been demonstrated by Briggs *et al.* (1986). Applications at the moment are limited, but this may change in the future, especially when non-classical starch sources are used, such as sorghum (Dale *et al.*, 1989; Delcour *et al.*, 1989).

Extrusion can also be applied to hops; this improves the conversion of α-acids to α-isoacids and results in a higher utilization of the bittering components (Omrod & Sharpe, 1989; Westwood & Crescenzi, 1989).

Sorghum. Sorghum is a traditional raw material for some African beverages such as Kaffir beer. The inability to cultivate barley in tropical countries and the restriction on barley and malt imports in some African countries stimulated research into the use of sorghum or malted sorghum for the production of lager beer. Sorghum malt differs from barley malt in its high gelatinization temperature (65–75 °C) and its low β-amylase content (Dufour & Mélotte, 1992; Taylor, 1992). Moreover, the limited cell-wall degradation leads to a poor wort and beer filtration (Okon & Uwaifo, 1985; Morrall *et al.*, 1986; Aisien, 1988; Aniche & Palmer, 1990). However, with an adapted mashing procedure and the use of commercial enzymes, sorghum malt can be used to produce an acceptable lager beer (Olatunji *et al.*, 1993). The use of unmalted but extruded sorghum as a cereal adjunct in brewing has also been studied (Dale *et al.*, 1989; Delcour *et al.*, 1989).

To a lesser extent, millet has also been studied as a possible malting crop in tropical countries (Nout & Davies, 1982; Aisien *et al.*, 1986; Malleshi & Desikachar, 1986; Singh *et al.*, 1988).

Modified hop extracts. Several companies sell hop extracts that are pre-isomerized under aqueous conditions. It is evident that the utilization of α-acids is improved by the use of these extracts. Modified isomerized hop extracts, where the α-isoacids are reduced, are also commercially available. The reduced α-isoacids have a higher bittering potential and improve the shelf-life stability of the beer in respect to the so-called sun-struck flavor—i.e., the deterioration of the flavor under the influence of sunlight. This feature is important when the beer is bottled in clear or green bottles that do not provide an adequate protection against sunlight. Moreover, the reduced α-isoacid extracts have an important foam-stabilizing capacity—as do normal pre-isomerized hop extracts, although to a lesser extent (Clark *et al.*, 1991; Moir & Smith, 1995).

Smith and coworkers (1998) have attributed the foam stabilizing and lacing properties of hop to the isomerized derivative of adprehumulone.

A more detailed overview about advances in hop technology, including the breeding, has been published by Gardner (1997).

Genetically modified yeast strains. The evolution in genetics and molecular biology of yeasts has made it possible to adapt the yeast strain to the needs of the brewer. This approach could finally result in a simplification of the brewing process. All the important brewing groups have studied the possibilities of genetic modification of the brewing strains, and several interesting strains have been constructed (for an extensive review, see Iserentant, 1989). Several authors (Young, 1981; Hammond & Eckersley, 1984; Röcken, 1984; Sasaki *et al.*, 1984; Fukui *et al.*, 1985) described the transfer of the so-called "killer-factor" in yeast. The killer factor is a naturally occurring yeast toxin that kills nonresistant yeasts. Transfer of such a factor to a brewing yeast would help to avoid wild yeast contaminations of the brewing fermentations. Several of the resulting killer strains behaved identically to the parental brewing strains, in respect both to the fermentation characteristics and to the flavor profile of the final beer.

The transfer of amylolytic genes to a brewer's yeast has been another, extensively studied field. An amylolytic yeast strain would allow the production of a low-calorie beer without the addition of exogenous enzymes to convert dextrins in fermentable sugar. Some attempts have been made by mating (Emeis, 1971) and protoplast fusion (Hockney & Freeman, 1979; Barney *et al.*, 1980), but the more direct approach of the cloning of the amylolytic gene and its transfer to a brewer's yeast has been more successful. The amyloglucosidase gene of *S. diastaticus* has been transferred into brewing yeast by Meaden & Tubb (1985), Sakai *et al.* (1988), and Vakeria & Hinchliffe (1989). The resulting attenuation was higher than for the untransformed brewing control, but about 70 % of the dextrins remained unfermented because of a lack of α-(1,6)-debranching activity so that branched dextrins could not be hydrolyzed. The α-amylase and amyloglucosidase genes of *Schwanniomyces* have been expressed in brewing yeast by Strasser *et al.* (1988), Lancashire *et al.* (1989), and Van de Spiegle *et al.* (1990). The resulting strains are superattenuating without loss of their positive brewing-yeast characteristics.

To improve the filtration characteristics of the beer, strains have been constructed expressing the β-glucanase gene from *Bacillus subtilis* (Cantwell *et al.*, 1985; Hinchliffe & Box, 1985; Lancashire & Wilde, 1987) or the cellulase gene from *Trichoderma reesei* (Enari *et al.*, 1987).

Both Sone *et al.* (1987) and Penttilä *et al.* (1988) have cloned the α-acetolactate decarboxylase gene from *Enterobacter aerogenes* to speed up the reduction of diacetyl and to shorten the maturation time. The enzyme can transform α-acetolactate directly into acetoin, whereas the normal transformation by yeast is dependent upon the slow, spontaneous decarboxylation of the α-acetolactate. The yeast has been used on a pilot scale: expression of the activity allows a significant reduction of the production time without any detectable change in fermentation performance or in flavor of the final product (Inoue *et al.*, 1989; Suikho *et al.*, 1989). Similar results have been obtained with a yeast, transformed with the α-acetolactate decarboxylase of *Acetobacter aceti* (Tada *et al.*, 1995). A totally different approach has been proposed by Masschelein and coworkers (Dillemans *et al.*, 1987; Villaneuba *et al.*, 1990; Goossens *et al.*, 1991; Goossens *et al.*, 1993). They showed that diacetyl formation can be prevented by avoiding the accumulation of α-acetolactate. Increasing the activity of the rate-limiting step, the reductoisomerase, by increasing the copy number of the *ILV5* gene (Figure 3–1) results in a decrease in diacetyl production. This approach has the advantage that no bacterial DNA has to be introduced in the yeast.

Hansen & Kielland-Brandt (1995) describe the construction of yeast strains with increased sulfite production. The increased sulfite level is supposed to prevent oxidation of the packaged beer and to improve the flavor stability.

None of the genetically engineered strains are in industrial use, so far. This is not the result of technical shortcomings of the genetic constructions, but rather a hesitance of the brewers to use a strain that may be conceived as "not natural"

by the public. The recent concerns expressed in public opinion about genetically modified plants has certainly slowed down the introduction of genetically modified strains for industrial use. However, genetically modified strains may be used in the near future: an increasing familiarity with the genetic techniques will lead to an increased acceptance, and positive examples, in both the medical and the food fields, will facilitate the introduction of genetically engineered strains in brewing.

Wort Production

High pressure wort filtration. Filtration is often the rate-limiting step in the brewhouse. For years, the brewers have been looking for a fast filtration system with a high extraction yield that would give a wort quality comparable with the lauter tun. A first attempt was made by Van Waesberghe (1979), who developed a high-pressure mash filter. This filter, however, had several technical shortcomings and did not meet the requirements.

Hermia *et al.* (1987) developed a mash filter consisting of a hollow frame divided into two parts by two elastic membranes. The frame is inserted between two plates covered with a filter cloth. The membranes can be inflated by compressed air. The filter is filled at low pressure; before sparging, the remaining extract is removed by a precompression of the spent grain caused by a first inflation of the membranes. The filter cake is washed and, after this sparging, the membranes compress the spent grains at high pressure to remove the remaining liquid. Several industrial filters based on this principle have already been installed (Eyben *et al.*, 1989; Melis & Eyben, 1992). Improvements based on the same principle have been described (Nguyen, 1995). The filter has a short filtration cycle and produced a clear, high-quality wort at a high extraction yield. The spent grains are dry (between 28 and 38 % dry weight) and the filter can easily be automatized. Moreover, the filter allows the use of a very fine grist, so that the expensive roll mills can be replaced by a cheaper hammer mill. The use of a fine grist leads to a more efficient saccharification: it is quite possible that a generalized use of the high-pressure mash filter may result in a further simplification of the mashing process.

Wort boiling. Various methods have been devised to reduce the energy needs of the wort boiling process.

Calandria. The need for energy saving strongly stimulated the development of shorter boiling processes and energy recuperation systems. A first improvement of the wort boiling process was obtained by the use of an external heat exchanger or calandria. The wort is circulated through the heat exchanger, mostly by the use of a pump. The advantage of this system is that higher temperatures can be reached (106–110 °C), resulting in an improved hop utilization and a decreased boiling time.

Mechanical vapor compression. Mechanical vapor compression is a system that can be applied easily to any external boiling system (Hancock, 1985; Taki *et al.*, 1987). The vapors from the coppers are compressed; the compressed vapors have a condensation temperature above boiling wort and can serve as a heat source in the external boiler. The vapor recompression technique has been adapted to brew kettles with an internal cooker, too (Klein-Carl & Reichert, 1991).

Low pressure boiling. Another system designed to save energy is wort boiling with low counterpressure (Lenz, 1982; Herrman, 1985). A pressure-resistant wort kettle is essential; the wort is heated to boiling temperature with an external calandria and the temperature is further raised to about 110 °C. The wort is kept at this temperature for approximately 15 minutes, and the boiling phase is followed by a pressure release and a post–boiling phase of 10 minutes. Vapor compression during all stages of the boiling process leads to important energy savings.

Continuous high-temperature wort boiling. The continuous wort-boiling technology has been conceived to save steam and energy (Chantrell, 1983). The wort temperature is raised to 140 °C in three consecutive heat exchangers, and the wort is held at this temperature for 3

minutes. Then, the pressure is reduced via two expansion vessels and the vapors are used to heat the heat exchangers. The energy saving, compared with a conventional plant, is claimed to be 69 %.

Wort boiling with limited evaporation. Recently, the so-called Merlin system has been developed, in which the wort flows in a thin film over a conical heating surface. Due to the large area of the heating surface, the removal of the undesirable heating compounds is efficient and the total evaporation can be reduced to about 4 % (compared to the conventional 8 %), so that an energy saving up to 50 % can be obtained. Results of industrial scale brews using this system have been described by Weinzierl (1999).

Stripping. Another boiling system, where energy saving is obtained by more efficient removal of unwanted flavor compounds, is wort stripping (Seldeslachts, 1999). Steam is used in a stripping column to remove volatile compounds from the wort. A saving of up to 46 % of the energy consumption can be obtained.

High gravity brewing. High gravity brewing is a process where wort is brewed at a higher gravity than normal and where water is added afterward to dilute the product to the desired density. The advantage of the system is that smaller volumes can be used during the production so that the productivity of the installation can be increased. Normally, the wort is brewed at a gravity between 13–18 °Plato, but in some cases, even higher gravities can be used (very high gravity wort). Although in theory, the wort can be diluted to the desired density before fermentation, normally both wort production and fermentation are carried out at high gravity, to obtain the volumetric advantage both in the brewhouse and in the fermentation cellar. However, fermentation of high gravity worts may cause a slowing down of the fermentation process and will normally change the flavor pattern of the beer. Moreover, when the final beer is diluted with water, special attention has to be given to sterilization and degassing of the water to prevent unwanted contamination or oxidation of the end product. Due to the fact that the dilution reduces the CO_2 content of the diluted product, additional CO_2 has to be added.

A recent review about high gravity brewing has been published by Koukol (1997).

Fermentation and Maturation

Unitank fermentation (warm maturation). One of the consequences of the introduction of the cylindroconical fermentation vessel was the development of a short fermentation and maturation process for lager beer in one vessel. The fermentation starts at the same temperature as a conventional fermentation, or slightly higher. However, when about half of the extract is fermented, the temperature is raised to approximately 15 °C. This results in a faster diacetyl reduction so that a rapid maturation is obtained. The form of the tank allows easy removal of the sedimented yeast during the fermentation so that no yeast autolysis flavor is formed during the period at high maturation temperature. Thanks to the modified temperature profile, the whole process of fermentation and maturation is shortened to about 14 days.

Continuous fermentation. In the 1970s, several attempts were made to develop a continuous fermentation process for brewing (Ault *et al.*, 1969; Portno, 1978). Continuous fermentation would give an interesting increase in productivity, because the typical lag phase of a batch fermentation and the time loss between two batches can be avoided. Most of the attempts were not successful, mainly because of contamination problems. However, at least some industrial plants are still operating in a continuous way, without problems worth mentioning (Davies, 1988; Dunbar *et al.*, 1988). Whereas continuous fermentation is certainly not generally accepted, continuous yeast propagation is starting to find acceptance and is already used in several breweries.

Immobilization. Several research laboratories studied the possibilities of yeast immobilization for beer fermentation and maturation and tried to develop the system up to an industrial scale. Immobilization indeed has several benefits: the

high cell load allows an increased volumetric productivity, yeast growth is reduced so that the substrate utilization is improved, the yeast biomass can easily be removed from the beer, and the immobilized system facilitates continuous operation. A review of perspectives of immobilized cell technology in brewing has been recently published by Masschelein & Vandenbussche (1999).

Carriers and reactor design. Yeast immobilization can be realized by different methods, but gel entrapment or surface entrapment is most often used. Gel entrapment (e.g., calcium alginate beads) is often the method of choice for the laboratory, thanks to the ease with which the yeast-charged beads can be produced and the possibility of analyzing the yeast biomass by redissolving the beads. However, the gels lack mechanical resistance and, in most cases, more resistant surface-attachment matrices (e.g., glass or ceramic beads) are chosen for pilot and industrial-scale reactors. An overview of carriers used for yeast immobilization is given by Hayes *et al.* (1991).

The reactor design is a crucial parameter in the application of immobilization to beer fermentation. Fixed bed reactors are simple and easy to operate, but, in the case of the main fermentation, problems are encountered from the CO_2 production, which disturbs the bed structure. Moreover, because of the slower growth pattern of the yeast in an immobilized column, the beers contain higher levels of free amino acids (Curin *et al.*, 1987). Fluidized bed reactors are more difficult to handle, but the CO_2 removal is not a problem and they have the additional advantage of a better amino acid utilization by the yeast, which results in an improved flavor profile of the beer (Masschelein, 1987; Cop *et al.*, 1989).

Application to the main fermentation. One of the first applications of immobilized yeast to the main fermentation of brewing was described by Narziss & Hellich (1971): the yeast cells were retained by a yeast filter element. White & Portno (1978) described the first continuous brewing fermentation with immobilized yeast cells. They used a calcium alginate entrapment matrix in a packed bed reactor. Pardanova *et al.* (1982) proposed a similar packed bed reactor with calcium alginate beads. An adapted form of such a reactor has been described by Curin *et al.* (1987) for both discontinuous and continuous wort fermentation at a pilot scale with a capacity up to 90 Hl/week.

Godtfredsen *et al.* (1981) were able to produce a low-calorie beer using a yeast co-immobilized with an amyloglucosidase in calcium alginate beads in order to obtain both dextrin degradation and fermentation.

The main disadvantage of the gel-inclusion matrices used in those systems is that the beads are damaged by the yeast growth and the vigorous CO_2 production and, as a consequence, the yeast bleeds out of the fermenter. The use of other, mechanically stronger carriers can solve those problems. Linko & Kronlöf (1991) compared the performance of DEAE cellulose, ceramic beads, and glass beads as carriers during the main fermentation. When porous glass is used as a carrier, the flavor formation is stable and the beer quality is similar to that of a beer produced in a traditional fermentation. The same authors combined the use of an immobilized reactor with the use of a genetically modified α-acetolactate decarboxylase-producing yeast. In this system, the fermentation and maturation time is reduced to 2–6 days (Kronlöf & Linko, 1992).

Long-term experiments using immobilized yeast columns with porous glass beads have been described by Virkajärvi & Kronlöf (1998).

Application to maturation. Beer maturation in a traditional process is time consuming; shortening the process using immobilized yeast is an interesting alternative. Moreover, maturation with an immobilized yeast column is technically easier than the use of an immobilized system for the main fermentation: during maturation, both yeast growth and CO_2 production are limited. For these reasons, the application of immobilization to beer maturation has been very successful, and immobilized yeast columns are now used on an industrial scale.

Researchers at the Kirin brewery described a pilot installation (Nakanishi *et al.*, 1985, 1986; Onaka *et al.*, 1985) in which beer was passed in a continuous way over a calcium alginate entrapped yeast column, after an initial, aerobic, free-cell fermentation. The aerobic phase was intended to promote amino acid uptake and to limit the production of the unwanted flavor compound diacetyl. In later experiments, the alginate beads have been replaced by a ceramic carrier, which is more reliable (Ohno, personal communication).

Pajunen and coworkers (Pajunen *et al.*, 1987, 1991; Grönqvist *et al.*, 1989) developed an immobilized yeast reactor for continuous maturation of beer after a classical free-cell main fermentation. After the fermentation, the yeast is removed by centrifugation and the beer is heat treated to transform the heat-labile diacetyl precursor α-acetolactate into diacetyl. After this treatment, the beer is passed over a packed bed column consisting of yeast fixed on a DEAE-cellulose carrier. During this passage, the diacetyl is reduced to acetoin by the immobilized yeast. The procedure allows the maturation time to be shortened to a few hours, and the system is now used on an industrial scale in the Sinebrychoff brewery in Finland.

Low-alcohol beer. The interest in the production of low-alcohol beers (see below) opened a new application field for immobilized yeast. As in the case of maturation, yeast growth and CO_2 production are limited during the production of low-alcohol beer. Immobilization offers an advantage of high cell loading and flexibility in production that cannot be reached by a free-cell system.

Van de Winkel *et al.* (1991) chose a silicon carbide multichannel membrane to immobilize the yeast and develop a two-stage, external-loop reactor. The same reactor has been adapted to carry out the main fermentation (van de Winkel *et al.*, 1993). Aivasidis *et al.* (1991) proposed the use of glass beads in a fluidized bed reactor. The beer produced by this system was comparable with a low-alcohol beer produced in the classical way, in respect to both the analytical and the sensorial characteristics.

The Dutch brewery Bavaria immobilized yeast on a packed bed DEAE cellulose column for the industrial production of their alcohol-free beer (Meersman, 1992). A similar column is used for the immobilization of lactic acid bacteria. These bacteria are used to obtain a wort acidification as a first stage in the production process of the alcohol-free beer (Pittner *et al.*, 1993).

NEW PRODUCTS: LOW-ALCOHOL BEER, ALCOHOL-FREE BEER, AND ICE BEER

Low-Alcohol Beer and Alcohol-Free Beer

Several factors, such as the demand for healthy drinks, the perceived social effects of excessive alcohol consumption, and severe drunk-driving legislation, have caused considerable market growth of reduced-alcohol beers during the past few years. The terminology used for reduced-alcohol beers is not clear: names like light beer, low-alcohol beer, and alcohol-free beer have different meanings in different countries. We consider all the malt-based products, produced by a process specially intended to limit the alcohol content of the final product, as "reduced-alcohol beer." Where necessary, the alcohol content will be defined.

Several production processes have been proposed for reduced-alcohol beers. Those processes can be divided into two main groups, the first being a physical treatment of the beer in order to remove the ethanol produced, and the second an adaptation of the existing brewing and/or fermentation processes with the intention to limit the ethanol production. In general, the physical processes require specialized equipment and have an inherently higher production cost, whereas adaptation of the process normally can be carried out with the existing equipment of the brewery but results in a beer with a rather worty taste. Each process, however, has its own advantages and disadvantages. The most important processes are discussed in detail below. A review of special processes published

as US patents is given by Gonzales del Cueto (1992).

Physical Removal of Ethanol

The most important processes to remove ethanol from beer are distillation, vacuum distillation, evaporation, reversed osmosis, and dialysis. Detailed discussion of these methods and schedules of the installations can be found in Regan (1990), Lengnes (1990), and Stein (1993).

Distillation. Distillation is one of the oldest methods to produce reduced-alcohol beer. By cooking the beer under atmospheric pressure and diluting the concentrate with water up to the initial volume, a beer can be obtained with an alcohol percentage of 0.5 % volume. However, because of the high temperature needed, the beer has an unpleasant cooked character and the method is rarely used now.

Vacuum distillation. An improvement of the distillation process is obtained by applying a vacuum, so that much lower temperatures (50–60 °C) can be used. By this adaptation, the occurrence of the burned flavor can be avoided, but the beer loses several volatile flavor compounds with the ethanol. This problem can be solved by a two-step process in which, first, the esters and other volatile compounds are removed and then, in a second stage, the ethanol is stripped from the beer. The alcohol-free beer is cooled and mixed with the flavor compounds. By this procedure, beer with very low ethanol concentration can be obtained.

Evaporation. Evaporation by a thin-film evaporator is the most sophisticated form of the distillation techniques. The installation allows the use of low temperatures (between 30 °C and 40 °C) so that the thermal degradation of the beer is minimized. Beer with a very low alcohol percentage can be produced and the ethanol can easily be further concentrated by conventional distillation. However, one still needs to add a flavor "cocktail" to compensate for the loss in volatile aroma compounds.

Reversed osmosis. Reversed osmosis is fundamentally different from the techniques described above. Beer under high pressure (30 to 50 bar) is passed through a reactor with a semipermeable membrane. Water and low-molecular-weight compounds such as ethanol pass through the membrane while other compounds are retained. The process has the advantage that it can be carried out at low temperature, so that no thermal degradation of the beer occurs. The loss of flavor compounds is limited to compounds of low molecular weight. It is necessary to dilute the initial beer with water to compensate for the loss of water during the process. This dilution process helps to avoid the clogging of the membrane. A detailed description of the method is given by von Hodenberg (1991). Beer produced with this technique is much higher in esters and higher alcohols than beer produced by evaporation (Kavanagh *et al.*, 1991). However, it is not economically feasible with reversed osmosis to produce a beer with an alcohol percentage lower than 0.5 %.

Dialysis. Dialysis works on a principle similar to reversed osmosis, but the driving force is the concentration gradient rather than a high pressure. In theory, the technique is simpler and more attractive than reversed osmosis, but it is only recently that industrial installations based on this principle have been realized.

Beer is passed through a dialysis module with cellulose membranes; the dialysate passes through the reactor in counter current. Alcohol passes through the membrane in the dialysate, but the aroma compounds can be retained completely. An extensive description of the method can be found in Donhauser *et al.* (1991). The technique is simple and works at low temperature and low pressure. There is no dilution needed of the initial beer and the resulting product is of excellent quality. The dialysate can easily be distilled and yields a high-value alcohol. However, the application of dialysis is limited to the production of beers with an ethanol content higher than 0.5 %.

Adaptation of the Traditional Process

Although the physical removal of alcohol certainly has a number of advantages—the most

important being the low alcohol content that can be reached with some of the techniques—the main disadvantage is the specialized and costly equipment that is needed. For that reason, several breweries prefer to produce reduced-alcohol beer by an adaptation of the traditional process.

Adaptation of the mashing method. The simplest way to produce a low-alcohol beer is to start from a *low-gravity wort* produced by low gravity brewing or, normally, by a dilution of a normal gravity wort. Although this procedure is often used in combination with the limited fermentation technique (see below), fermentation of low-density wort on its own is not very successful because the procedure results not only in a low alcohol content, but also in a low flavor content. Several techniques have been proposed to solve this problem, the most elegant being *high-gravity brewing.* Fermentation of a high-gravity wort results in a beer in which the content of esters has disproportionally increased compared with the ethanol concentration. Dilution of such a beer to a reduced-alcohol beer results in a nearly normal flavor pattern. Colored malts (e.g., Munich) are often used to obtain a final beer with a normal color. The technique, however, is limited to the production of beers with 2 % alcohol or higher. For beers with a lower alcohol content (1 % or higher), *high-temperature mashing* can be used. By this process, the production of fermentable sugars is reduced by limiting the action of the saccharifying β-amylase. β-Amylase is more heat-labile than α-amylase: mashing at 80 °C inactivates the β-amylase, whereas the action of the α-amylase is unaffected. The method produces a wort with a high dextrin/fermentable sugar ratio; the resulting beer has a high dextrin content. A similar effect can be obtained by replacing a part of the malt by starch hydrolysates (added after inactivation of the enzymes). Adaptations of the mashing procedures to limit the β-amylase activity are often used in combination with the production of low-gravity wort and limited fermentation.

Other techniques, such as *cold-water extraction, spent-grain extraction*, and the *Barrell patent*, are discussed in Muller (1990) and Lengnes (1990).

Adaptation of the fermentation. S. ludwigii is a *special yeast strain* that ferments only glucose, fructose, and sucrose. This yeast ferments about 15 % of the normally fermentable sugars. The resulting beer is maltose rich, but the taste impression of maltose is less sweet than that of glucose or sucrose, so that the final beer is not too sweet. An alternative way to prevent the consumption of all fermentable sugars is *checked fermentation*—i.e., termination of the main fermentation (by rapid cooling and removal of the yeast) before a complete attenuation has been reached. The initial fermentation temperature is generally low and the oxygenation of the wort is limited to avoid diacetyl formation. As in the case of the use of a special yeast strain, the resulting maltose content of the final beer is high.

Cold contact is a special form of checked fermentation. It is the only form of limited fermentation that allows the production of a beer with an alcohol concentration below 0.05 %. The process has initially been described by Schur (1983). A standard wort is cooled to low temperature (between −1 °C and 0 °C) and pitched with yeast at high pitching rate. The yeast is left in contact with the wort for several days. Because of the low temperature, the metabolic activity of the yeast is low, but there is an adsorption of hop and wort compounds to the surface of the yeast and some reduction occurs of the carbonyl compounds from the wort that are responsible for the worty flavor.

An adaptation of this process, in which the yeast is immobilized (see above), is used by the Dutch brewery Bavaria. In this case, immobilization allows the use of very high yeast concentration without the risk of yeast autolysis that causes severe off-flavors in the beer.

Ice Beer

In recent years, Ice beer has become increasing popular in Northern America and in Europe. Although it is marketed as a new product, it

doesn't differ considerably from the classical lager beer. To produce Ice beer, matured beer is cooled down to −4 °C and stored for a period of about 2 weeks at a temperature between −4 °C and −2 °C. This maturation at low temperature results in a beer with a pleasant smooth taste.

CONCLUSION

The traditional brewery has changed: new technologies such as immobilization or even genetic engineering have found their application in the brewing industry. This evolution will speed up in the future. Some innovations in one part of the brewing process can have serious consequences for the rest of the process, resulting in a simplified brewing method or in higher productivity. The introduction of the mash filter allowed the utilization of finer grist, which led to better saccharification and may result in an adapted mashing process. The utilization of cylindroconical vessels allowed the introduction of the warm maturation and shortened the fermentation and maturation time of lager beers. Other technologies, such as immobilization, may lead to even more important changes.

The situation becomes even more complicated by the changing attitude of the consumer. The demand for healthy products resulted in the creation of low-calorie and low-alcohol beers. Brewers are experimenting with totally new products such as colorless beer (Tripp *et al.*, 1997) and beverages situated between beer and soft drinks. The new technologies are an indispensable tool in the development of those new products.

The brewer has to be aware of this evolution: the life cycle of a certain technology will become shorter and shorter. Investments will not last as long as before but should be conceived to be flexible so that an easy adaptation is possible to both new technologies and new products.

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4

Cidermaking

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HISTORY AND DEFINITION

Cider is generally regarded as a drink made from apples. In North America, the term "cider" generally refers to cloudy unpasteurized apple juice, unless qualified as "hard cider" to denote a fermented product. In Europe, however, terms such as cider, *cidre* (France), or *sidra* (Spain) are exclusively reserved for the fermented product, which is the topic of this chapter. German-speaking countries also produce cider, where the product is defined as *Apfelwein* or, colloquially, *Ebbelwoi* or *Viez*. A similar fruit wine (perry) is made throughout Europe on a much smaller scale from pear juice.

The greatest production of fermented cider is in England (*ca* 480 M liters p.a.), stretching in a band from the West Midlands counties of Hereford and Worcester through Gloucestershire to Somerset and Devon. Individual local operations are also found in East Anglia, Kent, and Sussex. Production in France is restricted to the northwestern areas of Normandy and Brittany and is *ca* 115 M liters p.a.. German cidermaking (*ca* 100 M liters p.a.) is centered mostly on a Trier/Frankfurt axis with some production in the southerly Swabian area. Smaller operations are found in northern Spain (*ca* 70 M liters p.a.), Ireland (*ca* 45 M liters p.a.), Belgium, Austria, Switzerland, Sweden, Finland, South Africa, Australia, Central and South America. In the United States, limited quantities of hard cider for beverage consumption are made in apple orcharding regions such as New England and upstate New York, Michigan, California, and the Pacific Northwest. In Canada, production is found in Quebec and in British Columbia. Fermented cider was common in North America from colonial times until the late 19th century when it went into considerable decline, but volumes are now rapidly increasing and were of the order of 12 M liters p.a. in 1998. However, it is worth noting that *ca* 100 M liters of fermented cider are also produced annually in North America for direct conversion to vinegar (Lea, 1989).

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Descriptions of cider and perry making in the Mediterranean basin are found in the works of the Roman writer Pliny during the first century AD (Pliny the Elder (reissue) 1967). Thereafter, its production appears to have moved north, so that cidermaking was well-established in France by the time of Charlemagne (9th century) and had probably been introduced into England from Normandy well before Duke William's conquest in 1066 (Revier, 1985; Roach, 1985). By the 17th and 18th centuries, its production in England had reached something of an art form and had become the subject of a number of learned discourses. Most famous among these are John Evelyn's Pomona (1664), Worlidge's Vinum Brittanicum (1678), and Knight's Treatise on Cider and Perry (1801). At this time, cider was regarded in some circles as a competitor to Rhine wines. Educated gentlemen such as Isaac Newton and Thomas Jefferson made cider on their country estates in both Great Britain and America (Browne, 1945; Macomber, 1955). During the 19th century the popularity and quality of cider declined, until it became little more than a cheap source of alcohol for itinerant farm workers and acquired its unfortunate "scrumpy" image. Increasingly since 1900, however, cider has prospered into new markets, and the last decade has seen an increase in sales against a generally static or declining consumption pattern for many other types of alcoholic drink. In Britain, more than 90 % of cider production is now concentrated in the hands of two large manufacturers. The balance is accounted for by about 6 independent companies with national distribution or significant "own label" business, followed by 100 or so "farmhouse" or "craft" operations with primarily local sales. In France, one company presently owns two-thirds of the business through a large number of traditional brand names. However, production by small-scale French factories (*ateliers artisanaux*) has increased to reach about 15–20 % of total cider sales.

Styles of cider are enormously diverse and not easily categorized. Presently in the United Kingdom the greatest sale of cider is a clear and carbonated product, in bottle or in can, with varying degrees of sweetness and with an alcohol content ranging from 1.2–8.5 % v/v (which are the UK legal limits, set by HM Customs and Excise Notice 162). Brand names are particularly important, since each company sells a wide range of products. The flavor is generally light by comparison with those available up to the 1970s. This follows an increasing trend toward chaptalization by addition of sugar syrups before fermentation, so that many UK ciders contain only 30–50 % apple juice equivalent in finished retail product (calculated from data given by Jarvis, 1993). New concepts such as high alcohol white ciders, which became popular during the 1990s, have their flavor deliberately stripped from them. Such products are marketing-led "designer drinks" and have no traditional counterparts. Other designer ciders are colored or flavored—e.g., with blackcurrant juice or malt liquor—or are "ice-filtered." History shows that most of these variants are ephemeral and may have a relatively short product life.

Ciders are also available on draught for pub consumption and are usually served chilled, like the lagers with which they are intended to compete. There is a small market for cloudy or naturally conditioned ciders, sold in casks or kegs both for home use and for pub consumption, particularly in the West Country. A number of smaller craft manufacturers also offer high-quality still or lightly carbonated full juice ciders with heavier and more complex flavor characteristics than the large producers—often these are based on a defined blend of known cider apples that forms a positive selling point. Sadly, in the tourist areas of Southwest England, acetic and poorly made ciders are still sold to unsuspecting visitors under the general title of "scrumpies" in an attempt to exploit an apparently traditional niche. Although the term "traditional" defies easy definition, there is a growing number of smaller makers who have taken the best of traditional and modern practice to produce ciders of genuine high quality that are perhaps similar to those of the 18th century zenith.

The diversity of UK cider styles reflects the relatively broad (and voluntary) British definition

as "a beverage obtained by the partial or complete fermentation of the juice of apples . . . or concentrated apple juice . . . with or without the addition before or after fermentation of sugar or potable water" (NACM, 1998). In France, Germany, and Spain, the definitions and practices are more restricted by specific vertical legislation, and the products within these countries are very different from those in Britain. Table 4–1 gives an outline comparison of European ciders.

French consumers expect cider made in France to be a sparkling beverage, mostly bright with a low alcohol content together with residual sugar, and characterized by sweetness and by tannic and apple-like flavors. German and Swiss ciders are slightly higher in alcohol and are relatively dry and acidic to an English or French palate. In Spain, mainly in Asturias, there is a preference for a distinct vinegar-like flavor that would be regarded as excessively acetic by other European consumers. In Asturias, too, the presentation of the cider and its foaming properties as it is poured into the glass represent important quality attributes (Mangas *et al.*, 1999). In France, a specific style of chaptalized cider (*cidre anglais*) is now permitted, but it must not be called cider and it is marketed as *boisson fermentée à base de pommes*. The reasons for some of these differences have a technological origin that will become apparent later. Because of this great diversity of cider styles, hopes of producing a harmonized EU definition of cider are thankfully unlikely ever to be successful.

It will be evident that cider is in effect an apple wine, and good practice in both the cider making and winemaking industries is closely similar, but there is much less technological affinity between cidermaking and beer brewing than is often supposed. It is therefore ironic that, in the United Kingdom at least, cider is marketed to compete directly with beer and sold in similar fashion. While the scientific literature of brewing and winemaking is vast, with technical journals and research institutes dedicated to both, the world literature on cidermaking is scant indeed. Much of it originated from the Long Ashton Research Station (LARS), near Bristol, United Kingdom,

Table 4–1 Typical Legislative Differences between Ciders in the United Kingdom, France, Germany, and Spain

Fermentable sugar (and concentrate) addition	
UK	Permitted *ad lib*
F	Not permitted, but concentrates may be used up to 50 %
D	Permitted to raise SG up to 1.055 maximum
ES	Not permitted
Alcohol levels (actual)	
UK	1.2–8.5 %
F	1.5 % minimum, 3 % maximum for *cidre doux*
D	5 % minimum
ES	4 % minimum, 4.5 % minimum for *sidra natural*
Acid addition	
UK	Malic, citric, tartaric, lactic permitted *ad lib*
F	Citric, malic only (maximum 5 g/l)
D	Lactic only (maximum 3 g/l)
ES	Tartaric, citric only (maximum 2 g/l)
Permitted sweeteners	
UK	Sugars and all artificial sweeteners permitted *ad lib*
F	Apple juice only permitted. Residual juice sugar varies from < 28 g/l (*brut*) to > 35 g/l (*doux*)
D	Sugar only maximum 10 g/l
ES	Sugar only maximum 80 g/l total (*dulce*); nil for *sidra natural*
Permitted coloring	
UK	All food colors permitted *ad lib*
F	Cochineal and caramel permitted
D	Small amounts of caramel only
ES	Caramel only
Permitted preservatives	
UK	Sulfite and sorbate only
F	Sulfite only
D	Sulfite and sorbate only
ES	Sulfite and sorbate only
Sugar-free dry extract (minimum)	
UK	No longer specified
F	16 g/l; 18 g/l (*cidre bouché*)
D	18 g/l
ES	13 g/l; 14 g/l (*sidra natural*)

Note: This table should not be taken as a definitive statement of the legal position.

which opened in 1903 as a cider research institute and closed that part of its work in 1986 when its resources were switched by government into arable crops research. However, the present success of the UK industry is largely attributable to the underpinning research conducted at LARS during those years. Much of the knowledge acquired over that time was authoritatively reviewed by Beech & Davenport (1970), Beech (1972a, 1972b), Beech & Carr (1977), and more recently by Beech (1993). Other reviews include those by Charley (from Warcollier 1949), Wallace & Marsh (1953), Pollard & Beech (1957), Schanderl *et al.* (1981), Proulx & Nichols (1980), Downing (1989), and Jarvis (1993, 2001). Although there is no longer direct support from UK government for cider research, the Pershore College near Worcester maintains a "Centre of Excellence" for cider with a particular brief to help the competitiveness of small-scale producers. In France, the INRA station at Le Rheu, near Rennes, supports a small state-funded program of cider research. In Germany, Switzerland, and Austria, scientific expertise in cidermaking derives from the state-funded wine research institutes at Geisenheim, Trier, Wädenswil, and Klosterneuberg. In Spain, the provincial authorities of Asturias on the northern Atlantic coast maintain a cider research department at Villaviciosa (Suarez & Picinelli, 2001). In the United States, small state-funded cider programs also exist—e.g., at the New York Agriculture Experiment Station (Cornell University).

RAW MATERIALS

Cider Apples

Apples are the primary raw material for cidermaking. The traditional classification for English cider apples dates from Barker's early work at LARS but is still a very useful guideline today (Table 4–2). The traditional French classification is similar, being based on total phenolic and acid determinations from laboratory-pressed juice. This French classification is now being renewed in a research program aimed at quantifying the individual native phenolic materials found in the fruits themselves.

Table 4–2 Classification of cider apples

	Acid (%)	*Tannin (%)*
Sharp	> 0.45	< 0.2
Bittersharp	> 0.45	> 0.2
Bittersweet	< 0.45	> 0.2
Sweet	< 0.45	< 0.2

Not all ciders are made from true cider apples—i.e., those grown for no other purpose—and many modern English ciders have a high proportion of dessert and culinary outgrades (particularly Bramley), or are reinforced with apple juice concentrate bought on the world market. Some English cidermaking areas, typically those in Norfolk, Kent, and Sussex, have always utilized dessert and culinary fruit rather than the specific cider varieties favored in the West Country. French cider apples are similar to those in England, although the names are unfamiliar—e.g., *Bedan* and *Kermerrien* (bittersweets), *Petit Jaune* and *Judor* (sharps). In Asturias, it is principally sharp and medium bittersweet cultivars that are used (Dapena *et al.*, 1988). In Central Europe, there are no true bittersweet apples but a number of *Mostäpfeln* such as *Trierer Weinapfel*, *Bohnapfel*, *Borsdorfer*, and *Blauacher* (Scholten, 1992). More than 300 French cider cultivars are listed and described in considerable detail in a recent volume by Bore & Fleckinger (1997). Morgan & Richards (1993) list and briefly describe 72 English cider cultivars among a list of around 2,000 apple types maintained in the Brogdale Horticultural Trust collection. Over 80 Somerset cider cultivars are pictured and described by Copas (2001).

True cider cultivars, because they are selected solely for this purpose, have a number of advantages to the cidermaker. Chief among these are:

- potentially high sugar levels (up to 15 % is not uncommon)
- range of acidities from 0.1–1.0 %

- fibrous structure to make pressing easier and juice yields higher
- the ability to mature for several weeks in storage without losing texture while starch converts to sugar
- a high tannin (polyphenol) level for body and "mouthfeel" in the finished product.

In some cases, cider fruit is also characterized by vintage quality, which is of particular concern to the small traditional producer. Vintage-quality fruit gives generally more complex and interesting flavors to the cider than does bulk fruit. However, the vintage cultivars have generally lower yields and are in some cases more difficult to grow. Typical UK cultivars (bulk and vintage) are given in Table 4–3. Further descriptions are given in Williams & Child (1965), Williams (1987), and Morgan & Richards (1993). Cider orcharding is a specialized business and can differ markedly from dessert fruit growing. Fruit size and finish are not important, but ease of mechanical harvesting is. Most modern cider orchards are of "bush" trees grown as a center-leader hedgerow wall for easy access by harvesting machinery. The trees are planted at *ca* 300 per acre rather than *ca* 30 per acre, which was usual for the standard (long-stemmed) trees found in traditional orchards. Some new orchards of standard trees are now being planted with regional grant-aid in the United Kingdom, for their landscape value as well as for cider production. Many cider cultivars are strongly biennial in their cropping—for the United Kingdom as a whole, biennial patterns may become established for several years at a time due to climatic factors. For example, between 1975 and 1986, all odd years were "off" and all even years were "on." Biennial bearing can be controlled by mechanical or chemical thinning of flowers or fruitlets during the "on" year. Modern cider orcharding practice has been reviewed in detail in a book edited by Williams (1988), and by Copas and Umpleby (2002).

It is rare for cider to be made of a single cultivar apple only. This is partly because the balance of sugar, acid, and tannin required for a successful product is difficult to achieve from any single cultivar (with the possible exception of some bittersharps such as Kingston Black and Stoke Red), and so a blend to achieve the appropriate balance is nearly always necessary (see Table 4–4). In addition, orcharding considerations

Table 4–3 Typical cider apple cultivars

	Early season	*Mid/late season*
Sharp/Bittersharp	Breakwells Seedling	Brown's Apple
	Backwell Red*	Frederick*
		Crimson King*
		Kingston Black*
	Foxwhelp	Stoke Red*
Bittersweet	Ashton Bitter	Dabinett*
	Ellis Bitter	Chisel Jersey
	Major*	Harry Masters Jersey*
	Tremlett's Bitter	Yarlington Mill*
	Taylors	Michelin
		Vilberie
		Medaille d'Or*
Sweet		Sweet Coppin*
		Sweet Alford*
		Northwood*

*Denotes vintage quality cultivars.

Table 4–4 Composition of "ideal" cider apple juice

Fructose (g/100 ml)	7–11
Glucose (g/100 ml)	1.5–3.0
Sucrose (g/100 ml)	2–4.5
Sorbitol (g/100 ml)	0.2–1.0
Starch	Nil (but up to 2 % may be present in unmatured fruit)
Pectin (g/100 ml)	0.1–1
Amino acids (mg/l)	500–2000 (of which asparagine/aspartic acid forms *ca.* 90 %)
Potassium (mg/l)	1200
pH	3.3–3.8
Titratable acidity to pH 8.1 as malic acid (g/100 ml)	0.3–0.5
Chlorogenic acid (mg/l)	300–700
Phloridzin (mg/l)	100–200
Epicatechin and procyanidins (mg/l)	1000–1500

such as the need for cross-pollination and a spread of harvesting period dictate the growth of relatively mixed orchards. Most large cider companies maintain a mixture of orchards under their own direct control as well as having contracts with outside growers. However, there are few incentives for freelance cider orcharding, since the fruit is unusable for any other purpose if market requirements change, and in a glut year the open-market price of fruit can drop dramatically. The newer craft cidermakers, though they may start with fruit from existing orchards, are tending where possible to establish orchards of preferred cultivars under their own control. In France, the major factories are supplied from specialized cider orchards growing about 15–20 preferred cultivars, as in England. However, significant supplies of older varieties still exist in France and continue to be used. Taking France, England, and Spain as a whole, the total area dedicated exclusively to cider orcharding in those countries now amounts to some 18,000 hectares (AICV, 2000).

For the most part, the gross composition of cider fruit is typically that of any apple (see Table 4–4). It is noteworthy, however, that juices from standard trees in old orchards contain generally far less soluble nitrogen than do juices from intensively cultivated bush orchards (particularly those in their early years). This reflects the nutrient status of the trees and can have a direct bearing on fermentation behavior and final cider quality, as described later. It has also been shown that the total polyphenol levels are inversely related to the nutrient status of the tree (Lea & Beech, 1978).

A distinguishing feature of true cider fruit, particularly French and English bittersweets, is the relatively high concentration of these polyphenols, loosely known as "tannin," which confers bitterness and astringency on the finished beverage. Although modern ciders are generally lower in tannin than in the past, it still makes an important contribution to overall mouthfeel of the beverage and prevents it from becoming too insipid. The polyphenols also inhibit the breakdown of fruit pectin, which makes bittersweet apple pulp less slimy and therefore easier to press. For many years the nature of the tannin was obscure, but it has now been established as a range of oligomeric procyanidins based on a flavanoid (-)epicatechin structure. In cider apple juice, a range of oligomers up to the heptamer is present. In addition to the procyanidins, two other classes of polyphenol, which are not true tannins, are also present. These are the phenolic acids (chlorogenic and *p*-coumaroyl quinic), together with phloretin gluco-

side (phloridzin) and the xyloglucoside (Lea, 1978, 1982, 1984). Examples of these components are shown in Figure 4–1. Levels of all these components in bittersweet cider cultivars may be tenfold higher than in dessert apples. It is not entirely clear why this should be so, but since they are characteristic also of wild *Malus* species it is probable that they were not specifically bred out over many generations (as they were from dessert apples). Since the polyphenols make a major contribution to flavor, color, and pressability and also have weak antimicrobial properties, there was every reason to retain them.

In France, a breeding program began in the 1990s aimed at providing new bittersweet cultivars that exhibit good orchard behavior. In support of this, new research work on the phenolics of cider apples has shown that the fruits of some sharp cultivars contain the same amounts of total phenolics as those of bittersweet cultivars. They differ by containing more highly polymerized procyanidins (e.g., in the cultivars *Guillevic* and *Avrolles*) and by a lack of the simple catechins and a predominance of the phenolic acids (Sanoner *et al.*, 1999). This work has also demonstrated that cider apples may contain highly polymeric procyanidins that are not present in the juice and are only extractable into aqueous acetone (Guyot *et al.*, 1997, 1998). In Germany, high-tannin cider fruit is not available, but the sorb-apple fruits (*Speierling*) of *Sorbus domestica* are added to some blends to provide this character (Ritter *et al.*, 1993).

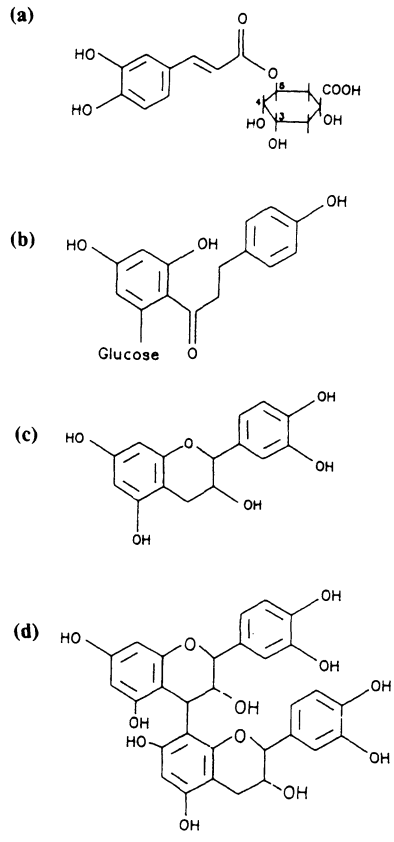


Figure 4–1 Typical phenolic components in cider apples (from Lea, 1991). (a) Chlorogenic acid; (b) phloridzin; (c) (-)epicatechin; (d) procyanidin B2.

Apple juice concentrate (AJC) is now widely used in English cidermaking and is permissible also to a limited extent in France. The advantage of a 70 ° Brix concentrate to the cidermaker is that it may be stored for years or months with relatively little deterioration compared to fresh juice and can be bought at a spot-price on the world market in almost any required specification. True bittersweet concentrate is obviously in very short supply, however, and is only available from France at a premium price, or is sometimes prepared in-house in the United Kingdom. The perceived advantages of AJC can be so great, particularly if just-in-time business practices are followed and retention of finished product is to be minimized, that some companies work almost entirely from this source. This extends even as far as concentrating local juice in season rather than using any of it fresh. Most companies, however, use a mix of fresh juice and re-diluted AJC as required. Other fermentable sugars from cane, beet, or hydrolyzed corn syrup are also commonly used as adjuncts in modern UK cidermaking.

Milling and Pressing

Where fresh fruit is used, milling and pressing to extract the juice is an indispensable operation (Downes, 1994). The fruit should be fully ripe

and is generally stored for a few weeks after harvest so that all the starch can be converted into sugar. Traditionally, milling was delayed until the fruit would retain the impression of a thumbprint when squeezed in the hand! The apples must be sorted and washed before milling to eliminate rotten fruit and orchard debris, which have adverse effects on microbiological status and ultimate cider quality. In the past, fruit was crushed to a pulp by stone or wooden rollers, followed by pressing in a "rack and cloth" or "pack" press. In this technique, layers of pulp are enclosed in woven synthetic cloths and alternated with thin wooden racks to form a "cheese," which is then subjected to mechanical pressure to extract the juice (formerly straw was used to separate the layers). The cheese is then stripped down and the pomace may be wetted with *ca* 10 % its own weight of water and repressed to obtain a further yield of slightly weaker juice. Eventually the pomace is discarded, sometimes being used for animal feed or pectin production. This method of juice extraction has persisted from medieval times and is still used in small-scale operations today, using modern hydraulic equipment. Juice yields can be very high (75 % or greater) with low levels of suspended solids. However, the process is very labor intensive and is economically unsuited to large operations.

In Spain, a specific form of press has been developed by the Asturian industry. These presses constitute a vertical stainless steel cylinder set upon a tray. The cylinder is filled with about 15 tons of milled pulp to a cake height of about 1.7 meters. This is then slowly pressed by a descending ram over a period of 16–60 hours, during which the height reduces to about 0.25 meters. During this operation the ram may be raised several times to allow the press cake to be broken up to improve drainage and juice yield.

In the United Kingdom, most major cider producers nowadays use a high-speed grater mill that feeds a Bucher-Guyer HP horizontal piston press. This is a semi-continuous system in which pulp is enclosed in a compressible chamber through which run a multitude of flexible juice ducts enclosed in porous nylon socks. When the piston is compressed, juice is forced out along the ducts and is collected outside the chamber. The piston is then withdrawn and the dry pomace falls away before another charge of pulp is added. The system is largely automated and one operator can control the pressing of several tons of fruit per hour. It is also flexible enough to cope with fruit in poor condition, which may need light continued pressure, and with a second extraction of pomace by water leaching. Continuous belt presses are a possible alternative to the piston press. Although they are much cheaper to purchase, they are not as flexible in operation and are usually only suited to firm fruit in good condition. Once the juice is prepared, by whatever means, it is coarsely screened and run off to tanks of fiberglass, high-density polyethylene, stainless steel, or (less commonly) wood for prefermentation blending and additions.

An alternative traditional procedure is worthy of description because of the scientific principles that it embodies, and because in modified form it is still used in France, although effectively obsolete in England. This is known in France as *maceration et cuvage* (Revier, 1985; Beech, 1993). The pulp is milled in the normal way and is then packed more or less firmly into barrels to stand at 5 °C for 24–48 hours. During this time, large amounts of pectin are solubilized from the middle lamella of the apple cell walls and leach out into the juice. This pectin is also partly demethylated by the native pectin methyl esterase (PME) activity of the fruit. At the same time, polyphenol oxidase (PPO) acts on the fruit "tannin" in the presence of air to develop soluble color. If this oxidation continues further, the oxidized polyphenols (particularly procyanidins) are tanned back onto the pulp and the level of soluble polyphenols and color may be diminished. The skilled cidermaker may thus control the color and the bitterness/astringency of the juice by varying the packing density in the barrels to control the access of the pulp-bound PPO to air and thereby the overall degree of oxidation (Figure 4–2). Different cultivars will vary in their response to this treatment, depending on their

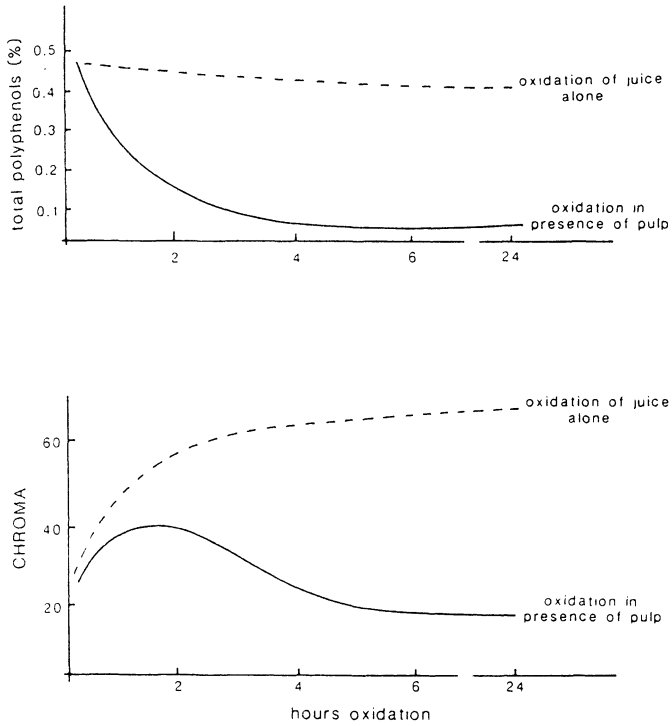


Figure 4–2 Color changes in oxidizing apple juice and pulp (from Lea, 1994). Changes in total polyphenols are also shown at the top of this figure.

maturity, the level of substrate, and the level of PPO activity (which is increased in juices of higher pH).

Once *cuvage* is completed, the juice is pressed out in the normal way and run to further barrels for the second stage of the process, the *défécation* (known as "keeving" in English). By maintaining the juice at around 5 °C, PME activity will slowly continue, whereas significant yeast growth will not. Over a few days, therefore, the demethylated pectate anion will combine with juice cations (principally calcium, protein, and asparagine) to form a gel that rises as the so-called *chapeau brun* to the top of the barrel. This is buoyed up by small bubbles of CO_2 from the incipient fermentation. Some complexed material will also sediment to the bottom, leaving a clear liquid layer in the middle. If the keeving is successful, this clear layer is carefully siphoned or pumped away to a further tank for fermentation. If unsuccessful, and yeast growth overtakes PME activity, a turbulent white head (*chapeau blanc*) is formed that signifies premature fermentation and consequent failure. The process is extremely skilled, although it can be made somewhat more reliable by the addition of 500 ppm calcium chloride (or a mixture of 300 ppm powdered chalk and 400 ppm common salt) before keeving. The added calcium helps the pectate gel to form while the chloride controls the growth of fermenting yeast. A further refinement of the process is to add a fungal PME to boost the weak natural activity in the fruit. Such an enzyme is now available commercially (as *Rapidase CPE* or *Klercidre*) to the industry in France, although it must be very carefully prepared since the slightest trace of polygalacturonase activity will cleave the macromolecular pectate and prevent

the gel from forming (Baron & Drilleau, 1982; Grassin & Fauquembergue, 1994).

The traditional keeving process described above is a static one, relying on spontaneous flotation of the *chapeau* to the top of the vat. In some French factories, a dynamic keeving process is now used. After two days' initial demethylation with added enzyme, the juice is pressurized with nitrogen, dosed with calcium chloride, and transferred to a continuous flotation tank. The calcium pectate gel that forms *in situ* is lifted to the top of the tank by the bubbles of nitrogen that adhere to it. The *chapeau* is continuously removed by a scraper to leave a clear juice underneath that is then racked into another vessel for fermentation.

The point of the keeving procedure is threefold. It produces a pectin-free juice that benefits the clarity of the final cider, it controls both color and tannin flavor, and it reduces the yeast and amino nitrogen content of the juice in order to retard the subsequent fermentation. In the context of French cidermaking, as described later, this is critical in retaining unfermented sugar for a naturally sweet product.

Juice Additions

Before fermentation, the must has to be prepared accordingly. In modern English cidermaking, this consists of blending the fermentable sugar sources (juice, AJC, and glucose syrups) to the required level. This may be as high as SG 1.080–1.100 to give a final alcohol of 10–12 % (or, exceptionally, up to 15 %), which is then diluted before retail sale. Nutrients are also added to ensure a complete and speedy fermentation to dryness, unlike the traditional procedure described above where care is taken that nutrients are removed from the juice. Apple juices contain considerably less free amino nitrogen than do grape musts and beer worts, which can place a severe limit on yeast growth. It is therefore usual to bring the level up to *ca* 100 mg nitrogen per liter, which is achieved typically by the addition of 250 ppm ammonium sulfate or phosphate. Vitamins for yeast growth are usually limiting in cider juices too, and so thiamine at 0.2 ppm is also recommended (thiamine is destroyed by sulfite and so must not be added at the same time as SO_2). Pantothenate (2.5 ppm), pyridoxine (1 ppm), and biotin (7.5 ppb) may be useful, too. These additions are particularly important if the must is made up with fermentable adjuncts (which do not contain any nutrients) or with AJC. In the latter case, much of the original amino nitrogen and nitrogenous vitamins are lost by the Maillard reaction with fructose that takes place during concentrate storage. Considerable losses (up to 50 % over three months) have been recorded by numerous authors (Lea, 1994).

It was demonstrated by Lüthi (1958) that the Maillard reaction produces a number of oxygen and nitrogen heterocyclic compounds that are strongly inhibitory to yeast. Among these is 5-hydroxymethyl furfural (HMF), although most of the inhibitors remain poorly characterized and HMF is probably most useful as an indicator of a whole range of related inhibitors. The yeast therefore needs assistance to overcome these inhibitors, and a good supply of nutrient and growth factors (often from a proprietary yeast autolysate) is therefore valuable. In severe cases, concentrates can be treated with activated charcoal to reduce the HMF levels before fermentation begins. Generally, yeast inhibition is a reflection of AJC quality, since proper storage conditions (4 °C) will minimize Maillard reaction and inhibitor formation. More recent work has, however, cast doubt on the practical significance of yeast inhibition by AJC, since the HMF levels recorded by Lüthi at *ca* 1000 ppm are much higher than those found in modern vacuum concentrates at < 20 ppm (Jarvis *et al.*, 1995.)

If clarified concentrates and adjuncts are to be fermented, a source of insoluble solids is often helpful. This allows the yeast cells a solid surface on which to rest, and from which ethanol and CO_2 can be liberated to the medium. Otherwise the yeast tends to compact at the bottom of the vat and a thin layer of these toxic end-products builds up around each cell, so that metabolic activity slowly ceases. There is therefore a case,

as in white wine fermentation (Ewart, this book), for allowing the addition of bentonite at about 0.5 % to the must before fermentation (Ough & Groat, 1978). This also aids the subsequent clarification of the cider.

Many cidermakers will also routinely add a pectolytic enzyme preparation prior to fermentation of fresh juice (AJC is, of course, already depectinized during manufacture). While this may not always be strictly necessary—since fresh juice contains PME activity and yeast contains a polygalacturonase, which together will act to remove the pectin—it is a wise precaution. If undegraded pectin persists at the end of fermentation, it is much more difficult to clarify in the presence of alcohol and can lead to intractable hazes. Pectolytic enzymes are sometimes added initially to the fruit pulp, if cull apples such as Cox are in use, to enhance pressability and to increase yield as well (Lea, 1991, 1994).

The most significant adjunct in modern UK cidermaking, as in white-wine making, is sulfur dioxide, the modern version of the 17th century sulfur candle. When originally introduced by LARS in the 1950s, its main role was to control the growth of acetic and lactic acid bacteria and to suppress the activity of yeasts other than *Saccharomyces* while their natural population slowly multiplied to dominate the fermentation. Nowadays, with the ready availability of dried active wine yeasts that can provide a massive inoculum within hours, it is tempting to omit the addition of SO_2, in an attempt to cut down on total sulfite usage or, in the case of ciders for canning, where little sulfite can be tolerated. This has often proved to be a false economy, however, leading to a proliferation of spoilage bacteria that generate off-flavors or that block membrane filters in final processing.

As described elsewhere in this book, the effectiveness of SO_2 is pH dependent since it is only the undissociated form (so-called molecular SO_2) that has antimicrobial properties. Hence cider juices should always be brought below pH 3.8 by the addition of malic acid before SO_2 addition, and the amount to add should be reckoned from Table 4–5. With healthy fruit containing only small amounts of sulfite-binding components, this should leave sufficient free SO_2 to provide an effective sterilization before the addition of a yeast inoculum 12 hours later (Figure 4–3). If the original fruit is in poor condition, it may contain large amounts of 5-ketofructose or diketogluconic acid from bacterial activity that will bind most of the added SO_2 and reduce its effectiveness (Burroughs & Sparks, 1964, 1973). Oxidized ascorbic acid, native to the apple, will degrade to l-xylosone, which is also a strong sulfite binder. Modern juices made up from depectinized apple juice concentrate contain relatively large amounts of free galacturonic acid. Although this is only a weak sulfite binder, its effect becomes significant at the high concentrations (thousands of ppm) that are present (Lea *et al.*, 2000; Jarvis & Lea, 2000).

Table 4–5 SO_2 Addition required to cider apple juices

pH	*Addition required (mg/l)*
3.0–3.3	75
3.3–3.5	100
3.5–3.8	150

Juices of pH > 3.8 (as in many full bittersweets) should be brought down to this value by blending or acid addition and 150 ppm SO_2 then added.

FERMENTATION

Yeast Selection

In traditional cidermaking, no external source of yeast is added. However, since the apples themselves contain a mixed yeast microflora that may be in the order of 5×10^4 cells/g stored fruit, spontaneous fermentation will commence within a few hours if the temperature of the juice is above 10 °C (Beech, 1993). Even if the fruit is well washed to remove superficial orchard contamination, as it should be, the internal fruit microflora together with inocula from pressing cloths and equipment can give yeast counts up to

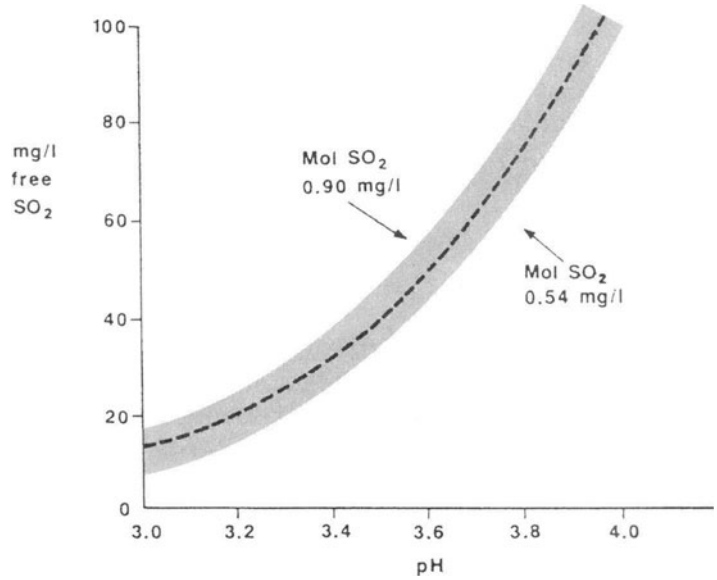


Figure 4–3 Antimicrobial level of free SO_2 in cider apple juice. The amount of free SO_2 that should be present after standing overnight is given by the shaded area.

10^6 cells/ml juice as it comes from the press. Experience with Bucher-Guyer HP mills and presses, fully sterilized just before use, shows that yeast counts of *ca* 10^4 per ml are the minimum that can be achieved in even the most fastidious commercial operation.

The yeast species present are a diverse collection. In studies at LARS over many years, Beech and colleagues identified the major species as *Candida pulcherrima* (now known as *Metschnikowia pulcherrima*), species of *Pichia*, *Torulopsis*, *Hansenula*, and *Kloeckera apiculata* (now known as *Hanseniospora valbyensis*). Strong fermenters such as *Saccharomyces cerevisiae* (*uvarum*) were not major constituents of the natural yeast microflora of the apples themselves, and the presence of *Saccharomyces* in the juice owed more to contamination from press cloths and factory equipment, where the inoculum appeared to persist from season to season.

In a traditional cider fermentation, therefore, where no yeast is added and no sulfite is used, the first few days are dominated by the non-*Saccharomyces* spp., which multiply quickly to produce a rapid evolution of gas and alcohol. They also generate a distinctive range of flavors, characterized by ethyl acetate, butyrate, and related esters. As the alcohol level rises (2–4 %), these initial fermenters begin to die out and the microbial succession is taken over by *Saccharomyces uvarum*. This yeast completes the conversion of all the sugar to alcohol and the generation of a more wine-like flavor. Once the *Saccharomyces* have exhausted all the available sugar, the final alcohol level is unlikely to exceed 8 % or so from single-strength juice. This can leave the product at the mercy of aerobic (film) yeasts (*Candida* or *Pichia* species), which may complete the unwanted conversion of alcohol to carbon dioxide and water unless the barrels are kept completely filled. Bacterial infection may, of course, also occur at this time.

If SO_2 is added to the initial juice, the non-*Saccharomyces* yeasts and most bacteria are suppressed or killed. This allows the *Saccharomyces* spp. to multiply after a lag phase of several days, and the fermentation then proceeds to dryness with a more homogeneous and benign microflora

than in the case of an unsulfited juice. Secondary infection is also less likely. This type of "semi-natural" fermentation was initially encouraged by Evelyn (1664), who recommended the use of sulfur candles burnt in the barrels just before the juice was added, and became the standard LARS recommendation from the early 1950s.

Nowadays, however, few cidermakers in the United Kingdom wait for the naturally selected *Saccharomyces* to establish themselves. Since the 1960s, specific cultured yeasts have been added to cider fermentations. Initially, these were often isolated originally from the cider factories themselves by the company microbiologists, and were propagated on slope cultures and grown up to provide a specific inoculum of "house" yeast. Other companies made use of known wine yeasts from research stations worldwide—for many years, strains such as Champagne Epernay, Geisenheim GEl, and Australian Wine Yeast 350R were popular. Apart from their ability to multiply quickly and to dominate a fermentation, they were recommended because of their freedom from taint or hydrogen sulfide production and for their ability to flocculate compactly at the end of fermentation.

Since the 1980s, however, the use of active dried wine yeast has become almost universal in the mainstream UK cider industry, as the commercial technology of preparing and storing such yeasts has been perfected. Typical strains employed are Uvaferm CM and BC (a Montrachet yeast via Germany and California and a Champagne *S. bayanus*, respectively), Lalvin EC1118 (another Champagne *S. bayanus* with killer factor) and Siha Number 3 (*S. uvarum* from a German vineyard). The use of a mixed inoculum of *S. uvarum* and *S. bayanus* is a widespread practice, on the grounds that the first yeast provides a speedy start but the second will cope better with the fermentation to dryness of the high-alcohol bases that are now common throughout the industry. These dried yeasts require no pre-propagation and are simply hydrated in warm water before pitching directly into the juice.

However, given the relatively high alcohol production required and the nature of the musts to be fermented in modern factory cidermaking, a period of deliberate aerobic yeast incubation may be essential for sterol synthesis and subsequent fermentation success. The aerobic phase, as in white-wine making, may take place either during the preparation of the yeast inoculum or during the early phase of fermentation (Ewart, this book). The vitality and viability of cultured cider yeasts under high stress conditions have recently been investigated (Seward *et al.*, 1996; Dinsdale *et al.*, 1999).

Traditional cidermakers, or those who are hoping to reestablish tradition, do not necessarily follow suit on yeast inoculation and may prefer some element of the natural microflora to remain. In Germany, there has been some concern that fermentations dominated entirely by *Saccharomyces* are lacking in estery cider character (the so-called *Apiculatus-ton*), and that the role of *Kloeckera apiculata* (*Hanseniospora valbyensis*) is important (Schanderl *et al.*, 1981; Scholten, 1992). Similarly, in France, the need for a mixed microflora is regarded as axiomatic, and recent experimentation has focused on mixed inocula of, for example, *Metschnikowia pulcherrima* and *S. uvarum* in an attempt to produce a complex and traditional flavor but under closer microbiological control (Bizeau *et al.*, 1992). Le Quere & Drilleau (1996) compared single and mixed-culture experimental ciders with commercial French ciders, using Principal Components Analysis of 26 key flavor volatiles assayed by GC. The experimental ciders fermented with a specific mixed microflora of *Saccharomyces uvarum* and *Hanseniospora valbyensis* were closer to the commercial ciders than when fermented with a single strain of yeast. They were not organoleptically evaluated, however.

As noted above when discussing juice preparation, French practice before and during fermentation differs markedly from English. Whereas keeving has no place in UK factory cidermaking, the French industry retains the process in a modernized form. The juice is kept cool after the addition of calcium chloride and commercial PME to encourage the formation of the *chapeau brun*. The juice is then clarified by centrifugation or tangential ultrafiltration into

tanks for an initial (natural) fermentation that lasts for one to two weeks. No sulfiting is used at this stage. The action of keeving followed by clarification reduces the nutrient level by at least 50 % and also effects a total reduction of the yeast microflora down to 10^3 cells/ml so that a relatively slow fermentation is ensured (Beech & Davenport, 1970). This is regarded as important, not only from the viewpoint of overall flavor development but also because French ciders must retain a proportion of their natural sugar. The ciders are centrifuged from the lees at a sugar level of 80 g/l for ciders intended to be sweet and 40 g/l for other ciders. A portion of these part-fermented ciders is then kept cool (3–4 °C) to arrest the fermentation as far as possible—if the sugar loss exceeds 1 g/l per month, the ciders are further centrifuged to remove the yeast crop and to inhibit the fermentation even more. These sweet ciders are then blended before sale with dryer ciders that have been allowed to continue their fermentation at ambient temperature with a typical sugar loss of 5 g/l per month. Everything is done to ensure that a slow fermentation continues for as long as possible (Revier, 1985; Drilleau, 1988, 1989).

Modern English practice is almost completely the opposite. The juices are prepared and inoculated as described above, and then a rapid and complete fermentation to absolute dryness is encouraged. Although in most cases there is no formal temperature control, a range of 15–25 °C is considered desirable. Thus, a portion of the fermenting juice is sometimes warmed to 25 °C by pumping through an external heat exchanger if it is slow to start or to finish. Most large UK cidermakers take the view that a complete fermentation to 10–12 % alcohol in as little as two weeks is a desirable objective. However, this attitude is not universally held, since the flavor quality and stability of the finished ciders can be compromised under such stringent conditions.

Malo-lactic Fermentation

Traditional ciders are very frequently subject to a malo-lactic fermentation. As in wines, the major desirable organism effecting this change appears to be the heterofermentative coccus *Leuconostoc oenos*, although other *Lactobacillus* spp. may also be present (Beech & Carr, 1977; Carr, 1983, 1987; Salih *et al.*, 1988). It is favored by a lack of sulfiting during fermentation and storage and by a certain amount of nutrient release from yeast autolysis when the cider stands unracked on its lees. In French cidermaking, where the primary fermentation is very slow, the malo-lactic change may occur concurrently with the yeast fermentation (Drilleau, 1992). In Spain, the long pressing time and the high temperature lead to bacterial and yeast growth commencing together during pressing. The juices ferment to dryness over 20–30 days, during which time the yeast and malo-lactic fermentations take place together. It is probable that the distinctively acetic flavor of Asturian ciders develops due to the further metabolism of lactate to acetate by lactic acid bacteria rather than by the action of *Acetobacter* during this period (Herrero *et al.*, 1999a, 1999b). In UK cidermaking, the malo-lactic change is most likely to occur once the primary yeast fermentation has finished and the cider is in bulk store.

The most obvious external feature of the malo-lactic change is the decarboxylation of malic to lactic acid and the consequent evolution of gas. In traditional cidermaking, this process often occurred with the advent of warmer weather in springtime and coincided with the flowering period of the trees. This gave rise to the belief that the cider and the trees were somehow working in sympathy! The acidity also falls and the flavor becomes rounded and more complex. Unfortunately, since this fermentation is inhibited at low pH, those ciders that might benefit most from acidity reduction are also those in which it is least likely to occur. Conversely, those ciders in which the malo-lactic fermentation takes place most readily are those in which it is often least welcome because of the pH rise that accompanies it. (As a rule of thumb, ciders above pH 3.8 are at increasing risk of bacterial or film-yeast spoilage and cannot easily be protected by sulfiting, since too little molecular SO_2 is available from the equilibrium at this pH.)

Work in France in recent years has shown that the malo-lactic fermentation can be encouraged by an appropriate inoculum of *L. oenos* into maturing ciders. The appearance of L-lactic acid is associated with the desirable aspects of malic acid metabolism—unfortunately, the appearance of D-lactic and acetic acids follows closely behind and is associated with undesirable flavor aspects (the so-called *piqûre lactique*). It has proved difficult to restrict the organisms to the desired L-lactic change, although a low bacterial inoculum and a high native polyphenol content appear to be of benefit (Salih *et al.*, 1987; Drilleau, 1992). The use of immobilized *L. oenos* with concurrent yeast fermentation in ciders has been investigated and appears to offer some commercial potential (Cabranes & Mangas, 1996; Cabranes *et al.*, 1998; Scott & O'Reilly, 1996; Nedovic *et al.,* 2000).

In modern UK factory cidermaking, the malo-lactic fermentation is generally regarded as a nuisance and is not encouraged. In any case, the prevailing conditions do not favor it, since sulfite is generally used before and after fermentation and the ciders do not stand on their yeast lees for long. Nonetheless, spoilage of stored ciders by rod-shaped lactic acid bacteria is not uncommon and often manifests itself nowadays by blockage of membrane filters during final packaging. However, the organisms involved, in this case, are not those that are associated with the traditionally desirable effect of the malo-lactic change.

Sulfite Binding

The binding of added SO_2 to juice carbonyls has already been mentioned above. Among these binders are 5-ketofructose from rotten fruit, L-xylosone from ascorbic acid, and galacturonic acid from pectin. A further (and usually the principal) source of sulfite binders in cider is generated during fermentation by the normal process of glycolysis and the operation of the Krebs cycle (Whiting, 1976). Pyruvate, α-ketoglutarate, and acetaldehyde are all essential metabolic intermediates in the production of ethanol by yeast. However, they are all carbonyls that bind to SO_2, and the amounts remaining at the end of fermentation will impact directly on the efficiency of any sulfite that is added to the cider for storage (Burroughs & Sparks, 1964, 1973). Acetaldehyde is by far the strongest binder, and until all this component is bound, no free sulfite can in practice remain in the cider. The other carbonyls bind less strongly and hence can coexist partly unbound in equilibrium with free SO_2. The fate of SO_2 added to cider or wine is shown diagrammatically in Figure 4–4. The percentage of cider carbonyls that are bound at a given level of free SO_2 is given in Table 4–6.

The carbonyl-bound sulfite has little antimicrobial action and yet it is determined as part of the total SO_2 when legislative limits are to be complied with. Given the constant pressure to reduce the total amount of SO_2 that is added to beverages, it is in the cidermaker's interest to ensure that the bound sulfite represents as little of the total as possible. This can be achieved only by minimizing the amounts of sulfite-binding carbonyls.

It is known that the addition of thiamine, for instance, will reduce the production of pyruvate and α-ketoglutarate during fermentation, since thiamine is an essential co-factor in the conversion of pyruvate to ethanol. It is also known that acetaldehyde production is reduced by added pantothenate. Ironically, the production of these binders is actually increased somewhat when fermentations are conducted in the presence of SO_2 (Beech, 1993). Juices fermented in the presence of large amounts (*ca* 300 ppm) of ascorbic acid produce excessively high levels of all three major carbonyls (up to 1000 ppm total), although the mechanism for this is not clear. It is also known that the malo-lactic fermentation can help to reduce sulfite binding capacity because of loss of pyruvate.

A new HPLC technique for the direct analysis of sulfite-binding carbonyls in cider has recently been devised (Lea *et al.*, 2000). Using this procedure, Jarvis & Lea (2000) measured the observed and predicted sulfite binding power of 12 commercial ciders and of 9 cider *Saccharomyces* strains fermented under various experi-

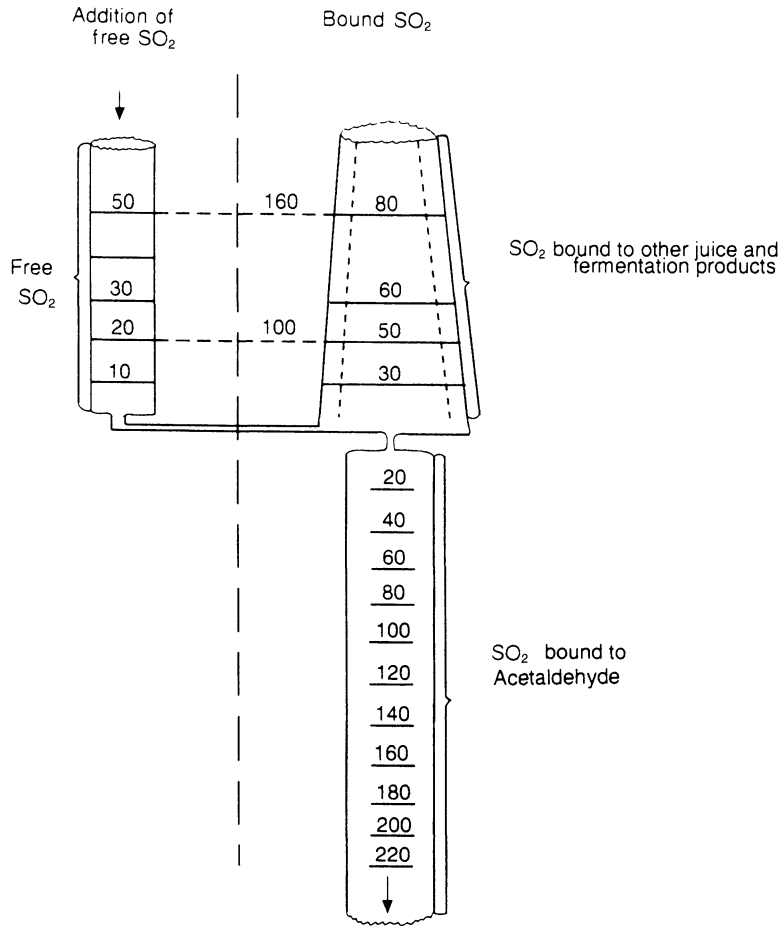


Figure 4–4 Fate of SO_2 in cider and wine. As free SO_2 is added to the system (i.e., to the left-hand limb of the diagram), it is consumed by the acetaldehyde present, shown by the bottom right-hand limb. Not until all the acetaldehyde is bound (i.e., the bottom right-hand limb is full) can an equilibrium be established between other components (top right-hand limb) and the free SO_2 required. Typical figures are shown (in mg/l) but the actual concentrations will depend on the amounts of binding substances present in each batch. (From Jakob, 1991).

mental conditions. They found that not all the sulfite-binding power of the commercial ciders could necessarily be accounted for by the known carbonyls. Cider yeast strains were shown to vary over a twofold range in their production of metabolic carbonyls and hence in their contribution to sulfite binding. For some yeasts, but not all, the production of carbonyls could be halved by nutrient and vitamin additions. The yeasts with the greatest sulfite binding capacity were also those with the greatest endogenous production of sulfite from sulfate, increasing its level by *ca* 50 ppm during fermentation. Clearly the selection of a yeast and its nutrient requirements is a key feature in minimizing the contribution of fermentation to the sulfite binding capacity of a cider. However, Jarvis & Lea (2000) also demonstrated that the presence of microbially generated carbonyls as contaminants in the original juice may still be a matter for concern and could account for up to 25 % of the binding power of a cider.

Table 4–6 Sulfite binding compounds in cider

	Percentage bound[a]	*Typical level in cider (ppm)*	*Bound SO_2 contribution (ppm)*[a]
Naturally present			
Glucose	0.11	7000	8
Galacturonic acid	4.4	1000	15
L-Xylosone	36	20	4
Acetaldehyde	99.8	25	35
Pyruvate	83	20	12
α-Ketoglutarate	58	15	4
From bacterial contamination			
5-Ketofructose	70	—	—
2,5-Diketogluconic acid	64	—	—
Overall bound SO_2			78
Total SO_2 (bound + free)			128

[a]Calculated for 50 ppm free SO_2.

Cider Color

The color of cider is determined by juice oxidation or degradation and, in fact, it is possible to make water-white high-tannin ciders if oxidation is completely inhibited (Lea & Timberlake, 1978; Lea, 1982). The effect of pulp and/or juice oxidation on juice color was described above (see Figure 4–2), and this sets the primary appearance of the juice that results from the quinoidal oxidation products of phloridzin, epicatechin, and the procyanidins (Goodenough & Lea, 1979; Goodenough *et al.*, 1983; Lea, 1984; Lea, 1991). This color will then be modified by the addition of sulfite. If added immediately after pressing, nearly all the color will be (chemically and visually) reduced as the sulfite binds to the quinoidal forms. If the sulfite is added later, however, less reduction in color will take place—presumably the quinones become more tightly cross-linked and less susceptible to nucleophilic addition and reduction. During yeast fermentation, however, the initial color diminishes by around 50 %. This is presumably because of the strong reductive power of yeasts, which readily reduce keto or carbonyl groups to hydroxyls with consequent loss of the chromophore. (Exposure to sterile air after fermentation will slowly regenerate the color.) These color changes are summarized in Figure 4–5.

The same considerations do not fully apply to AJC, however. In this case, much of the color results from Maillard browning during storage, rather than from phenolic oxidation. The carbonyl-amino chromophores that result are resistant to the reducing action of yeast, and so the color drops only 10 % or so during fermentation. Poor quality concentrate may therefore yield ciders with excessive "natural" color.

In commercial UK practice, cider color for any given product is now standardized by the addition of caramel or other permitted food color. By contrast, white ciders have had their color deliberately removed either before or after fermentation by the use of adsorbents such as activated charcoal. It is interesting to note that a maximum color level for UK ciders (40 EBC units) has been set by HM Customs and Excise quite distinct from that laid down in the Food Colours Regulations. This is to maintain the distinction between ciders and beers since they are taxed at different duty rates.

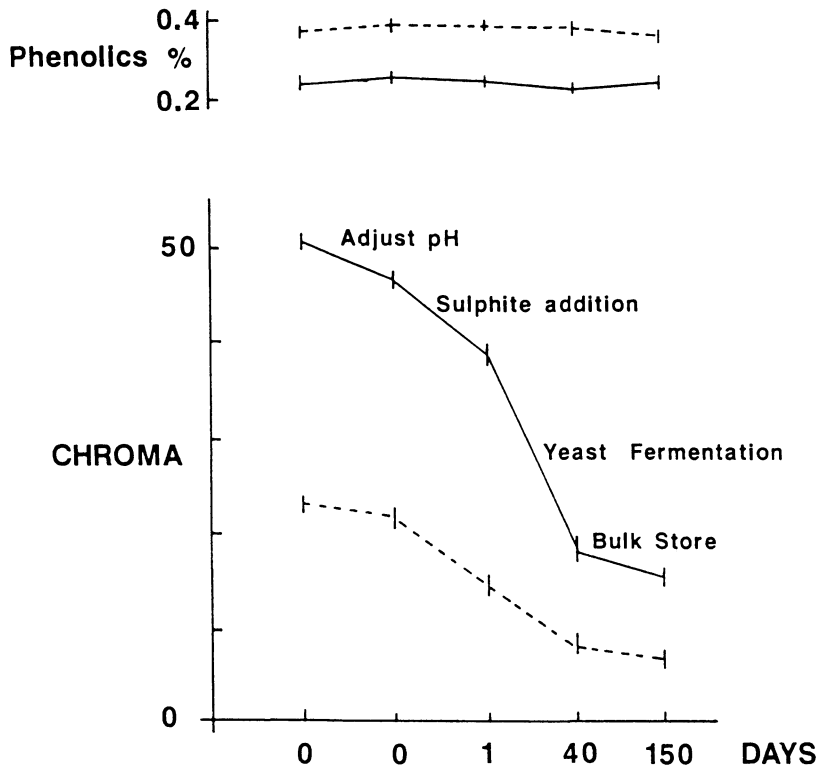


Figure 4–5 Color changes during cider manufacture. (—) oxidized on pulp 1 h; (--) pressed immediately.

Cider Flavor

As with any beverage, the flavor of cider is a combination of taste and aroma. Traditional English and French ciders made from bittersweet fruit have been distinguished by relatively high levels of bitterness and astringency caused by the procyanidins (tannin), as described in the Raw Materials section. The oligomeric procyanidins (n = 2–4) are more bitter ("hard tannin") than the polymeric procyanidins (n = 5–7), which are the more astringent ("soft tannin") (Peleg *et al.*, 1999). The levels are initially set by cultivar—thus Tremletts Bitter is more bitter than the astringent Vilberie although both fruits have the same level of procyanidins in total (Lea & Arnold, 1978, 1983). Juice-processing conditions (notably oxidation) also play a part in determining the final nonvolatile flavor, since oxidizing procyanidins become "tanned" onto the apple pulp and both bitterness and astringency markedly diminish (Lea, 1990). The change in phenolic levels during pulp or juice oxidation is shown in Table 4–7. It is generally accepted that oxidation of juice in the absence of pulp tends to change the balance from bitterness to astringency simply by increasing the molecular size of the procyanidins through random oxidative polymerization (Cole & Noble, this book). It has also been shown that the balance between the sensations of bitterness and astringency can be modified by the presence of alcohol, which tends to enhance the perception of bitterness and to suppress that of astringency even when they derive from the same molecule (Lea & Arnold, 1978). Furthermore, there is evi-

Table 4–7 Polyphenol levels in freshly pressed and oxidizing juices and pulps

(a) *Bramley*

Component	*Freshly pressed juice (15 min oxidation) (mg/l)*	*6 h oxidation after pressing (mg/l)*	*6 h oxidation on pulp before pressing (mg/l)*
Phenolic acids	373	253	196
Epicatechin	27	7	2
Procyanidin B2	14	0	0
Phloridzin	39	32	30
Oxidized procyanidins	309	165	17
Total	762	457	245

(b) *Dabinett*

Component	*Freshly pressed juice (15 min oxidation) (mg/l)*	*6 h oxidation after pressing (mg/l)*	*6 h oxidation on pulp before pressing (mg/l)*
Phenolic acids	686	564	109
Epicatechin	308	165	7
Procyanidin B2	306	163	8
Phloridzin	195	183	2
Oxidized procyanidins	788	1185	93
Total	2283	2260	219

dence that the flavor balance is also concentration dependent (Noble, 1990). Nowadays, the heavily tannic flavors of traditional ciders are much less in demand and the procyanidins are noticeable in modern factory ciders only as a part of the general mouthfeel.

The volatile flavor of cider is in most part qualitatively identical to that of all other fermented beverages and derives to a large extent from the yeast (Dürr, 1986; Cole & Noble, this book). As described earlier, yeast species and strain can have a significant effect on the generation of volatile flavor components, which is also subject to the effect of temperature, nutrient status, and so forth. Hence the quantitative flavor balance can vary. For instance, there is evidence that growth of *Hanseniospora valbyensis* is favored over *Saccharomyces* at low temperatures, with consequent flavor implications (Bilbao *et al.*, 1997). In controlled trials from a number of orchard sites in southern England reported by Barker (1943), it was also noted that the higher quality "vintage" cider cultivars demonstrated consistently lower juice nitrogen levels and hence slower fermentation rates when compared to cultivars of poorer quality. There is little doubt that the cool, slow mixed-microflora fermentation of an unclarified low-nutrient must will produce more flavor than is obtained from the fast fermentation of a high-nutrient must (though the desirability of this flavor to the consumer depends both on the cidermaker's skill and on his intended market).

The fermentation of a sterile sugar solution will readily produce a range of alcohols, aldehydes, and esters, all of which are found in ciders (Williams, 1975), but it is the balance between these components that partly typifies individual alcoholic beverages. Traditionally, ciders have been regarded as high in fusel alcohols, particularly 2-phenyl ethanol, which has often been

attributed to their low nutrient status. It is also known that higher fusel levels are generated from cloudy rather than clear juice fermentations (Beech, 1993; Vidrih & Hribar, 1999). The supposed hangover-generating properties of rough traditional ciders may perhaps be attributable to this and to high levels of ethyl acetate from the apiculate fermentation.

Detailed work by Williams's group over a number of years listed several hundred compounds as contributors to cider flavor (Williams & Tucknott, 1971, 1978; Williams, 1974; Williams *et al.*, 1978, 1980; Williams & May, 1981). The origin of many of them is still unclear. Some almost certainly arise from the fruit itself, particularly in the case of "vintage quality" cultivars such as Kingston Black and Sweet Coppin, and may give some further indication as to the nature of this elusive quality. Many will be generated by the yeast via well-known pathways, such as the formation of esters from the appropriate alcohols by the addition of acyl CoAs. However, the initial substrates may be fruit-specific. There is increasing evidence that apples, and indeed most fruits, contain nonvolatile glycosidic precursors that are hydrolyzed by enzymic action when the fruit is disrupted. Therefore, the high levels of 2-phenylethanol and its esters in ciders may not derive from *de novo* synthesis by the yeast (although this route is known), but from the presence of a glycosidically bound form in the fruit that is liberated and cleaved during fermentation (Schwab & Schreier, 1988, 1990).

One of the most interesting, and perhaps unique, volatile components of cider was described by Williams *et al.* (1987) and also by Hubert *et al.* (1990). Unpublished work in our own laboratories using "odor-port dilution analysis" showed that it has the lowest sensory threshold and therefore the greatest single odor contribution of any cider volatile. It also has a distinctive cidery aroma. Its molecular mass is 172, for which a number of structures were originally proposed including the acetal 1-ethoxyoct-5-en-1-ol (Williams *et al.*, 1987). In the first edition of this book, we suggested that it might instead be the dioxane resulting from the condensation of acetaldehyde with octane-1,3,-diol. The diol itself is a relatively unusual alcohol that is known to be present in apples and pears in a glycosidically bound form and that can reach levels of 100 ppm in stored fruit (Berger *et al.*, 1988; Beuerle & Schwab, 1997). Its unsaturated analogue 5-octene-1,3-diol also occurs in apples and would give a corresponding dioxane of molecular mass 170, for which we also had evidence.

Our hypothesis has since been confirmed by Dietrich *et al.* (1997). Using GC-MS and NMR techniques, they showed the existence of two dioxane enantiomers each in a 9:1 ratio in extracts from French ciders. The two main enantiomers of 2-methyl 4-pentyl-1,3-dioxan and its unsaturated analogue 2-methyl 4-(2-pentenyl) 1,3-dioxan were present in the cider at 22 and 8 ppm, respectively. In a subsequent paper, Kavvadias *et al.* (1999) demonstrated the existence in ciders of 17 further dioxanes formed from the same diols and a range of other fermentation carbonyls. It is almost certain that the two major dioxanes are present in ciders above their odor thresholds. Given the limited known distribution of the precursor diols in fruits, these "cidery" components result specifically from the action of alcoholic fermentation on apples and pears and could be largely responsible for the organoleptic distinction of cider and perry from other fermented beverages. Further work is needed, however, to confirm the sensory significance of these newly reported flavor components.

A further group of components results from the malo-lactic fermentation. It is well known that diacetyl is synthesized from pyruvate by *Leuconostoc* spp. and contributes positively to buttery flavors in wines and ciders (though often regarded as a defect in beers). Another group of flavors described as "spicy" and "phenolic" derives principally from the malo-lactic fermentation in bittersweet ciders. These are typified by ethyl phenol and ethyl catechol, which arise from hydrolysis, decarboxylation, and reduction of *p*-coumaroyl quinic and chlorogenic acids, respectively (Beech & Carr, 1977). Although these volatile phenols are not unique to cider, being found in whiskies too, they are distinctive con-

tributors at low levels to the characteristic bittersweet flavors of well-made traditional ciders from the West Country or northwestern France. At higher levels they contribute unpleasant 'barnyard' aromas, perhaps resulting from slow growth of the spoilage yeast *Brettanomyces* in cider during storage.

POST-FERMENTATION OPERATIONS

Racking and Storage

Once fermentation is complete, ciders are racked from the yeast lees for storage. Current practices vary widely. In some UK factories, racking and clarification take place as soon as possible for virtually immediate blending and packaging without any maturation. In others, the ciders remain on their lees for several weeks and are racked into inert tanks or oak vats for a maturation period of several months. Contact with air must of course be minimized, although carbon dioxide and nitrogen blanketing is not as widespread as in the white wine industry (Scott & Swaffield, 1998). During this time a malo-lactic fermentation may or may not be encouraged—if considered desirable, no SO_2 must be added during storage. Traditional maturation in old wooden vats is an active microbial process whose character probably arises from bacterial inocula that are resident within the pores of the wood (Swaffield *et al.*, 1997). This is quite distinct from the aging process by direct flavor transfer from new oak barrels that is now commonplace in the wine industry (Cole & Noble, this book).

Initial clarification may be performed by the natural settling of a well-flocculating yeast, by centrifugation, by fining, or by a combination of all three (filtration is generally left until the final product is ready for packaging). Typical fining agents are bentonite, gelatin, isinglass, or chitosan (a partially de-acetylated chitin prepared from crab-shell waste in North America or the Far East). Gelatin forms a floc with native tannin in the cider and brings down other suspended material by entrapment. Gelatin can also be used together with bentonite for similar effect. The use of the highly efficient gelatin/kieselsol system is widespread in Germany but less common in the United Kingdom, where instances of "overfining" and persistent gelatin hazes, therefore, sometimes occur. As a counsel of perfection, test-fining on a small scale should always be carried out to minimize the risk of overfining (Lea, 1994), but this procedure is often ignored and a standard amount of fining agent is added irrespective of actual requirements. Ciders made from cloudy juice concentrates can often prove extremely intractable to fine and may give persistent hazes.

Nearly all ciders are blended before sale. In a large factory, there may be dozens of different fermentations running or maturing concurrently, from different must sources and intended for different products. These form the base ciders from which blending is performed according to the cidermaker's requirements. At this point, a considerable amount of judgment and experience is needed. In most companies, the maturing vats will be tasted regularly so that the head cidermaker and his key staff know exactly what is available for blending according to the weekly production schedule. Since supermarket buyers and the companies' own marketing departments often dictate these schedules both for branded and own-label products at very short notice, such flexibility is vital in a large operation. Only the smaller cidermakers, not tied to supermarket contracts, now have the luxury of making their own decisions in this respect.

Blending involves more than just the ciders themselves. In the United Kingdom, water will be added to the high-alcohol bases to give the correct alcoholic strength for retail sale, together with additions of sugar and other sweeteners, malic or other acids, permitted food colors, preservatives, and carbonation. Generally, UK regulations permit for cider all those operations or additives that are allowed by EU "horizontal" food law. In France and Germany, specific "vertical" legislation applies to cider so that, for example, lactic acid is the only acidulant permitted in

Germany and a maximum level of 3 % alcohol is permitted for sweet ciders in France.

Final filtration may take place just before and after blending. Generally, powder filters or coarse disposable sheets are used to produce a bright product, followed by near-sterile sheet or membrane filtration (nominal 1–0.5 μm) to remove all yeasts and most bacteria. Most ciders are then pasteurized and/or carbonated into the final pack. In some cases, in-bottle or tunnel pasteurization of glass bottles or cans is still used. In other cases, the cider is hot filled into glass. With the increasing use of PET bottles in most large factories, HTST treatment in a flow-through pasteurizer and chiller is required, followed by near-aseptic filling conditions. Alternatively, cold aseptic filling after sterile membrane filtration (0.2 μm) is used. Cross-flow ultrafiltration systems are now becoming more widespread in the cider industry, despite occasional problems with membrane blockage and poor throughput for reasons covered later.

Nearly all cidermakers will aim to add 50 ppm of SO_2 at filling to give an equilibrium level of 30 ppm free SO_2 in the beverage. This depends on the level of sulfite binders in the cider, as described earlier. For cans, the total level of SO_2 compatible with the lacquer is often as little as 25 ppm. Otherwise, the base metal may be attacked if the lacquer fails, with the resultant formation of hydrogen sulfide in the pack. Ciders destined for canning are often specially fermented in the absence of sulfite throughout. Ascorbic acid is sometimes used for its antioxidant effect, but of course it has no antimicrobial activity. Sorbic acid, although permitted in ciders, is rarely used since it inhibits only yeast and is only fully effective in the presence of SO_2. If attacked by bacterial action, it can give geranium-like off-flavors caused by the production of 2-ethoxy-hex-3,5-diene.

Some smaller cidermakers bottle and sell their products completely dry without added sugar. In these cases no pasteurization is necessary, although sulfite is often added to preserve freshness. Other "farm-gate" operations sweeten bulk dry cider with sugar just before sale in polyethylene containers, but the shelf life of the product is then very limited and it must be kept refrigerated. There is a certain market for "naturally conditioned" ciders in kegs or small plastic barrels. These are generally produced from fully fermented dry ciders, to which an additional charge of sugar and flocculating yeast has then been added. The product is, of course, somewhat cloudy but may remain in good condition for many weeks because of the slow continued fermentation. True "champagne" ciders, prepared by fermentation in bottle followed by disgorgement of yeast from the neck, have been effectively absent from the UK market since the 1950s, although some craft cidermakers are attempting to revive the style. At the time of writing, the sale of such high quality ciders in the United Kingdom is effectively crippled by severe sparkling wine excise duties, which are far in excess of those applied to other styles of cider.

A current approach to natural conditioned bottled ciders by small makers in France relies on slow fermentation to a sugar level some 10 g/l higher than required for sale (e.g., 50 g/l for sale at 40 g/l). The ciders are blended, centrifuged, and filtered to near sterility. A small amount of active dried yeast is then added and the cider is bottled, the yeast being sufficient to allow a slight fermentation in the bottle so that the cider becomes sparkling. This approach to the natural in-bottle conditioning of sweet cider is only practicable after the slow fermentation of a nutrient-poor must and the removal of its initial yeast crop, so that excessive re-fermentation does not occur.

Storage Disorders

The classical microbiological disorder of stored bulk ciders is known as "cider sickness" or *framboisé* in French (Beech & Carr, 1977; Carr, 1987). This is caused by the bacterium *Zymomonas anaerobia*, which ferments sugar in bulk sweet ciders stored at pH values greater than 3.7. When first described by Barker in 1906 it was commonplace, but it is virtually unknown in English cidermaking today since the ciders are

generally at pH values below 3.5 and are never stored sweet. However, it is still occasionally encountered in France, where high pH bittersweet ciders undergo a natural arrested fermentation to leave them with considerable residual sugar. The features of cider sickness are a renewed and almost explosive fermentation, accompanied by a raspberry or banana-skin aroma and a dense white turbidity in the beverage. These have been attributed to acetaldehyde, which is produced at high levels by *Zymomonas*. The acetaldehyde reacts with the phenolic tannins to produce an insoluble aldehyde-phenol complex and consequent turbidity (the "Bakelite" reaction). The acetaldehyde also binds completely with any added SO_2 so that in practice the bacterium cannot be controlled by sulfiting. It is unlikely that the characteristic aroma derives entirely from acetaldehyde, since the pure compound does not smell of either banana or raspberry. It is more likely that minor quantities of other aroma components are formed but were not identifiable when this disorder was first described; it has not been re-investigated using modern gas chromatography techniques. The prevention of sickness is easy, simply following the rules given above, but its cure is not possible. The renewed fermentation is, therefore, allowed to take its course and the (insipid) dry cider may be blended-off to conceal its origins.

Drilleau (1976) described an alternative explanation of cider sickness originating from the work of Dupuy & Maugenet (1963), since *Zymomonas anaerobia* has not yet been found in French ciders. Under anaerobic conditions, the organism *Acetobacter rancens* will ferment D and L lactic acids into acetaldehyde, acetoin, and CO_2. Therefore, if the malo-lactic fermentation is prevented and hence no lactic acid is available, this form of cider sickness cannot occur. If it does take place, the sugar may remain unchanged, and therefore affected ciders may be cured by re-fermentation with added yeast to destroy the excess acetaldehyde. In this case, a characteristic, slightly "sick" aroma remains, indicating that acetaldehyde is not the only volatile involved in this disorder.

Another classical disorder, termed "ropiness," is also still encountered, especially in Spain (Duenes *et al.*, 1995; Fernandez *et al.*, 1996). This is caused by certain strains of lactic acid bacteria (*Lactobacillus* and *Leuconostoc* spp.) that synthesize a polymeric glucan (Carr, 1983, 1987). At low levels this increases the viscosity of the cider, and when poured it appears oily in texture with a detectable sheen. At higher concentrations of glucan, the texture thickens so that the cider moves as a slimy "rope" when poured from a bottle. The flavor is not much affected. If not too severe, ropy cider can be cured by agitating vigorously to break up the glucan chains, followed by the addition of 100 ppm SO_2 to prevent further growth.

Lactic acid bacteria may also break down glycerol, which is the major product of the yeast fermentation other than ethanol. Anaerobic degradation by *Lactobacillus brevis* and *L. collinoides* yields 3-hydroxypropanal, which can spontaneously dehydrate in acid solution to form propenal (otherwise known as acrolein) (Rentschler & Tanner, 1951). This can confer a bitter taste to ciders and an unacceptable pungent aroma when the cider is distilled, as in the production of Calvados.

Sub-acute ropiness caused by lactic acid bacteria is relatively common and is a frequent, though largely unrecognized, cause of membrane or ultrafilter blockage since (unlike depth filters) they have relatively little tolerance to the presence of small quantities of "coating" polysaccharides. We have identified a number of such cases in recent years where the blocking agent, once isolated and characterized, proved to be of this type. In some cases, the bacteria (both rods and *cocci*) could also be identified upstream of the membrane pre-filter, and the problem was traced back to inadequate sulfiting, which caused the bacteria to proliferate in storage.

Other related cases of filter blockage are attributable to mannans (which may derive from extracellular yeast polymers) or arabinans (from insufficiently degraded pectin side chains in AJC) (Brillouet *et al.*, 1996). It is likely that these phenomena have always existed, but have

only become manifest following the introduction of new technologies based upon submicron membranes or ultrafilters. There are considerable parallels between these and the similar situations in red wines described by Boulton (this book).

Microbiological problems arising from acetic acid bacteria (*Acetobacter*) or from osmotolerant yeasts arising from AJC (e.g., *Zygosaccharomyces bailli*) are generally fairly obvious. The latter organism is now endemic in modern commercial cider factories because of the use of AJC and because it is able to grow or to survive under conditions of low water activity. It can be a problem because of its resistance to SO_2 and, therefore, if it contaminates a sweetened finished product, there is a significant chance of renewed fermentation and the risk of exploding bottles.

Another sulfite-resistant spoilage yeast is often less well recognized since it grows slowly in sweetened bottled ciders to form large flaky clumps that do not necessarily appear to be yeastlike on initial examination. This is *Saccharomycodes ludwigii*, which originates from the cider fruit and displays particularly large cells (25 μm diameter). Macroscopically it is often mistaken for a so-called protein deposit.

True protein deposits in bottled ciders are actually very rare because the native protein content of apple juice is so low (*ca.* 100 ppm). Such deposits nearly always result from overfining at some point in production where excess gelatin has been added. Often this is further back in the production chain than the cidermaker realizes. Many apple juices that are used to prepare concentrate are fined with gelatin and kieselsol prior to concentration in their country of origin. If this is not done carefully, the concentrates when purchased may contain relatively large amounts of unstable protein still in the presence of colloidal silica. This will not be apparent in the concentrate itself, since the protective effect of the high solids prevents agglomeration and flocculation from occurring. After fermentation and dilution, however, the unstable protein may eventually precipitate to form a haze or a deposit. These are recognizable, after isolation and washing, by their content of silicon and sulfur, using techniques such as energy-dispersive X-ray microanalysis. The protein pattern may also be recognized by the use of Fourier transform infrared spectroscopy.

Many cider deposits also involve significant quantities of polyphenols, in conjunction with protein and polysaccharide. These are the classic chillhazes of traditional ciders, more obvious nowadays than in the past since ciders are more frequently served chilled and consumers expect to find a sparklingly bright product. Often the cause can be traced back to oxidation, where the oligomeric procyanidins have polymerized further in the presence of metals such as iron and copper (which are also usually detectable when the deposits are analyzed). Complexation with each other or with protein and pectin residues is then sufficient to "shock out" a haze or a deposit when the product is cooled. Even in the absence of protein or of significant oxidation, such hazes may still form at low pH as a result of breaking and re-forming of carbon-carbon bonds between the procyanidin units, leading to the slow buildup of random polymers that eventually drop out of solution. Since the parent unit (procyanidin B2) has a molecular weight of only 580, even the use of ultrafiltration through tight cut-off membranes will not necessarily prevent haze formation from occurring (Lea, 1994). SO_2 is, however, relatively effective, since it acts both as an antioxidant and as a blocking nucleophile to trap the carbonium ions that are formed during initial bond fission (Lea, 1989).

Flavor Disorders

Flavor taints in ciders may arise from adventitious contamination—e.g., the presence of naphthalene and related hydrocarbons in a situation where tarred rope had been stored adjacent to a cider keg. Such cases are impossible to predict but are often obvious after a flavor extract is prepared and analyzed by gas chromatography/mass spectroscopy, since the tainting compound will be of a structure never normally associated with

alcoholic beverages. However, many taints are endogenous or arise from an imbalance in the natural flavor profile resulting from microbiological action. For instance, ethyl phenol, ethyl catechol, and ethyl guaiacol are normal and desirable constituents of ciders at low levels but can become overt taints if unwanted bacterial action or *Brettanomyces* yeast generates large amounts from their nonvolatile precursors. A wide range of sulfidic and "woody" notes are associated with ciders and sometimes become regarded as taints. However, they appear to have extremely low thresholds (parts per trillion or less) and their nature remains unknown.

A frequent cider taint is that of "mousiness." This was extensively investigated by Tucknott at LARS (1977) and more recently by Heresztyn and colleagues in Australia (Strauss & Heresztyn, 1984; Craig & Heresztyn, 1984; Heresztyn, 1986). Current opinion is that isomers of 2-acetyl or ethyl tetrahydropyridine are the tainting species, generated possibly by the growth of *Lactobacillus* or *Brettanomyces* spp. under aerobic conditions in the presence of both lysine and ethanol. Similar components (particularly the 2-acetyl derivative) are generated thermally during the baking of bread, the precursors being synthesized from proline by the yeast (Grosch & Schieberle, 1991). In this case, they are not only desirable but indeed essential to the "fresh-baked" aroma, and they may also be responsible for the "bready" flavor of some beers. In ciders and wines, they are always regarded as objectionable, although their recognition depends on an interaction between cider and salivary pH. As bases, they exist in the salt form in ciders and are not detectable until converted to the free base (volatile) form in the mouth. Hence, mousiness is rarely detectable in the headspace aroma of ciders, and takes a few seconds to appear when the cider is tasted. In susceptible individuals, however (those with high pH in the oral cavity), the phenomenon is persistent and unpleasant. If the pH value of an affected cider is raised above 7, all the salt is converted to the volatile base and the mousy/bready character becomes detectable in the headspace. Analysis by odor-port gas chromatography in our own laboratories has confirmed that several closely related compounds are in fact present in "mousy" ciders.

A newly described taint in ciders is that caused by indole. This compound is well known in meat products, particularly pork, where it can form a part of the so-called boar taint and is derived from tryptophan breakdown (Wilkins, 1990). At very low levels it is also found in many flower aromas, and indeed it is often incorporated in soaps and perfumes for its floral attributes. At levels in excess of 200 parts per billion, however, its odor becomes increasingly fecal and unpleasant. Work in our own laboratories has identified indole as a relatively widespread taint in ciders, which may derive from an odorless precursor or salt since it often appears and disappears from bottled products. Almost certainly it is not derived from tryptophan, since this amino acid is virtually lacking in apple juice, and in ciders no trace has been found of skatole (3-methyl indole), which would be a necessary intermediate. Current belief is that it is generated *de novo* by the yeast from inorganic nitrogen during its own synthesis of tryptophan, rather than its breakdown. The factors favoring the synthesis of indole appear to be a low juice content and a low yeast pitching rate, coupled with a fast fermentation stimulated by high temperature and the addition of simple inorganic nutrients such as ammonium phosphate. Under these conditions, the yeast vitamin requirements are not adequately met from endogenous sources, and a specific deficiency in pyridoxine (a known co-factor in transamination reactions) appears to be the immediate cause of indole formation. Industry sources suggest that indole formation can therefore be suppressed by the addition of pyridoxine to the must at *ca* 1 ppm.

There are no adverse implications for human health from the microbial metabolites in ciders described in the preceding sections. Two areas of potential concern in fresh apple juice (often described as "apple cider" in the United States) are those of verocytoxin from *E. coli* O157:H7 and patulin from *Penicillium expansum*. They are not a risk in fermented ciders, since these organisms and/or their metabolites do not sur-

vive the fermentation process (Semanchek & Golden, 1996; Stinson *et al.*, 1978; Burroughs, 1977), although their initial presence in the juice should be regarded as an indicator of poor fruit handling practices that need to be remedied. The conversion of patulin to escladiol in fermenting ciders has recently been elucidated (Moss and Long, 2002).

CONCLUSION

Although a relatively minor alcoholic beverage in global terms, the production of cider has a long tradition over much of Europe, and is now finding increasing acceptance in other Western markets such as North America and Australia. Even the Far East is now subject to the first tentative steps in cider production and marketing by UK manufacturers. Styles of cider differ greatly, but they are increasingly influenced by technological advances made in other parts of the fermented beverage industry, so that it is now possible to understand and to control in broad terms the character of each particular product. This potential control applies over the whole industry, from mainstream chaptalized ciders through to full juice craft ciders. Enough scientific knowledge now exists about all aspects of cidermaking, such that the attainment of any particular style should be consistently achievable by anyone wishing to create it.

With this knowledge it should be possible to maintain and expand the diversity of the whole industry. There will undoubtedly be new cider styles devised to suit new markets—for instance, in Asia and North America. But the revival of craft ciders in the United Kingdom, or the maintenance of that tradition in France and Spain, should be welcomed and defended against the bland uniformity that threatens to overwhelm them. In the same way that the wine industry in both the Old and New World sees strength in its diversity of products, so should the cider industry worldwide celebrate the individual styles that it represents. In making both commercial and technical progress, and in developing new markets for cider, it is important not to lose sight of its traditions and its heritage as the fermented juice of apples in all their variety.

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5

White Wines

Andrew Ewart

WINE STYLES AND GRAPE VARIETIES

The wine styles produced in the New World countries have their origins in those wines that have evolved over an extended period of time in the traditional winegrowing regions of Europe. Whilst the European systems tend to be very specific about which grape varieties can be used, the New World winemaker is not so constrained and may use a range of varieties in the production of a particular wine style. This chapter covers white wine production primarily from a New World viewpoint, but good practice in Europe is nowadays often similar.

It is useful to classify the wine styles as follows:

- dry, white, floral and fruity wines
- medium-dry, white floral and fruity wines
- dry white full-bodied wines
- sweet white table wines

Dry, White, Floral and Fruity Wines

The models for the two main groupings here are the Riesling from Germany and the Traminer from Alsace in France. These wines typically have terpenes as major aroma and flavor contributors (Table 5–1). Other grape varieties used for this wine style include Frontignan and a number of Muscat-flavored varieties. A very strong breeding programme in Germany has seen a substantial number of new floral-type varieties grown, the most significant being Müller-Thurgau and Kerner. As a style, these wines typically have low to moderate alcohol (9–11 % v/v), high acidity (greater than 7.5 g/l as tartaric acid), low pH (less than pH 3.3) and an absence of malolactic aroma and flavor. Dry wines are generally classified as having less than 7.5 g/l residual sugar and table wines as having between 8 and 14 % (v/v) alcohol. It should be pointed out that Sauvignon blanc wines as typified by those produced in New Zealand also fit well into this category.

Medium-Dry, White, Floral and Fruity Wines

This style originates with the sweet white wines of Germany and, in particular, the wines of the Mosel district. *Spätlese, Auslese*, late picked and late harvest are all terms used to describe

Table 5–1 Classification of some grape varieties based on monoterpene content

Muscat varieties	*Non-muscat aromatic varieties*	*Varieties independent of monoterpenes for flavor*	
Canada Muscat	Traminer	Bacchus	Merlot
Muscat of Alexandria	Huxel	Cabernet Sauvignon	Nobling
Muscat à petits grains blancs	Kerner	Carignan	Rkaziteli
Moscato bianco del Piemonte	Morio Muskat	Chardonnay	Ruländer
Muscat Hamburg	Müller Thurgau	Chasselas	Sauvignon Blanc
Muscat Ottone	Riesling	Chenin Blanc	Semillon
Italia	Scheurebe	Cinsault	Shiraz
	Schönburger	Clairette	Sultana
	Siegerrebe	Dattier de Beyrouth	Terret
	Sylvaner	Doradillo	Trebbiano
	Würzer	Forta	Verdelho
		Grenache	Viognier

Williams *et al.* (1986).

wines in this category, which have residual sugars after fermentation in the range of 10–30 g/l. The wines should be fresh with a good acid balance.

Dry, White, Full-Bodied Wines

The classic wines of origin for this style are the Grand Cru whites of Burgundy, where Chardonnay is the specified variety. These wines have higher alcohol levels (13–14 % v/v), lower titratable acidity (6–7 g/l as tartaric acid) and higher pH values (< 3.5) than the floral and fruity wines. The style has oak aromas and flavors and the 'buttery' characteristics of a malolactic fermentation. Whilst Chardonnay has generally been the grape variety of choice in the New World, winemakers have been equally as successful producing this style using the varieties Semillon, Sauvignon Blanc and varying blends of all three. The fruit is harvested late and usually involves a degree of contact with oak either during or postfermentation.

Sweet, White Table Wines

This wine style is characterized by a residual sugar greater than 30 g/l and an acidity in the range of 8 to 10 g/l and a pH in the order of pH 3.3 to 3.7. These wines fall into two major groupings; (i) those produced by *Botrytis cinerea* infection and (ii) those produced by other techniques of sugar concentration. The botrytized sweet white wines are the most complex, the classic styles being the *Trockenbeerenauslese* of Germany and the Sauternes of France. The German wines tend to be low in alcohol (9–12 % v/v) and high in residual sugar (120–150 g/l). The French Sauternes, by comparison, have higher alcohol (around 14 % v/v), residual sugar ranging from 65–100 g/l and distinct new oak aroma and flavor characters in the wine (Table 5–2). The grape varieties used in the production of the traditional wines are Riesling, Semillon, Sauvignon Blanc and Muscadelle. With *Botrytis* infection, the grape varietal characters become lost and any variety may be used with similar results. However, varieties differ in their susceptibility to infection and this influences the degree of botrytis character in the final wine. The non-botrytized sweet white table wines are often made with Muscat flavored varieties or contain a proportion of Muscat Gordo Blanco (Muscat of Alexandra) juice to give the wine some distinctiveness. These wines are made by stopping the fermentation with residual sugar or back blending with conserved grape juice, or may be made from grapes partially dried on the vine or on mats on the ground.

Table 5-2 Analysis of sweet white table wines

Wine	*Country of origin*	*Residual sugar (g/l)*	*Glycerol (g/l)*	*Alcohol (g/l)*	*pH*	*Tartaric acid (g/l)*	*Total sulphur dioxide (mg/l)*
1975 Ch d'Yquem	France	100.9	20.2	14.1	3.50	7.6	244
1976 Joh Jos Prum Beerenauslese	Germany	121.7	11.1	6.8	3.28	7.1	318
1975 Ch Rieussec	France	77.9	14.7	14.1	3.48	7.3	334
1976 Heitz and Knod Beerenauslese	Germany	85.0	21.5	9.3	3.37	7.3	258
1978 Nederbury Edelcure	South Africa	173.5	12.5	10.9	3.86	8.6	106
1982 De Bortoli Botrytis Semillon	Australia	148	9.8	11.5	3.61	8.4	—
1983 Primo Estate Riesling	Australia	150	20.1	10.6	2.89	11.6	—

From S. Smith and Sons (Yalumba Wines).

IMPROVED PLANTING MATERIAL

Whilst there are a wide number of grape varieties suitable for producing the wine styles described above (Antcliffe, 1979; Galet, 1979; Dry and Gregory, 1988), considerable effort has been made worldwide to select improved vine material within a variety. This process of clonal selection has led to increased vine productivity and improved fruit composition in terms of sugar, acid and pH. From a wine quality point of view, it is important to understand what effect this has on wine aroma and flavor. Versini et al. (1989) indicated differing levels of grape flavor compounds in a selection of Traminer clones in Germany and Chardonnay clones in Italy. Selection should be based on both productivity and flavor. In the absence of flavor differences, the most productive vines should be selected. Ewart et al. (1993) report yield and compositional differences in selected clones of Sauvignon Blanc in South Australia but no significant differences in wine quality. The selection of improved plant material is in part the selection of disease-free material, but in order to end up with the best possible wine it is important to start with genetically superior vines.

THE VINEYARD AND HARVEST

The Vineyard

One of the shortfalls of the New World production philosophy has been the degree of specialization that has occurred. This has resulted in rapid advances in the two disciplines of Viticulture and Oenology but has to some extent broken the integral linkage between growing the grapes and making the wine. In order to achieve the best outcome it is essential for the winemaker to understand and have direct input in the production of the grapes. It is only in this way that he/she will end up with the grape quality required for the designated end use.

The winemaker is increasingly required to produce wines of varying style and to meet different price points in the market place. For the super premium end of the market, estimating and controlling grape yield is crucial to achieve varietal intensity and mouthfeel in the wines. Whilst yield is very important, the vine canopy architecture and particularly the degree of fruit exposure to sunlight can have a profound effect on the flavors produced.

Harvest

The optimum time of harvest is determined by the wine style being produced. For the 'fresh fruity' style, moderate alcohol, distinctive aroma and flavor with a crisp acid finish and no astringent phenolics are the key criteria. For the full-bodied wines, high alcohol, strong varietal flavor and complexity become the desirable attributes, which means harvesting at a later maturity.

In order to pick the grapes at the right stage of maturity, it is important that the oenologist takes an active role in sampling and monitoring the vineyard, as the composition and quality of the grapes will largely determine the outcome of his/her winemaking. Ideally, sampling should start 4 to 5 weeks before harvest, with the vineyard being sampled once a week initially and then twice a week as harvest approaches. It is important that the sample represents all the fruit on the vine and not just the exterior clusters which tend to be riper.

The objectives of the grower and the winemaker often differ. The growers wish to harvest as soon as possible to minimize loss caused by bird damage, disease or berry weight decrease, and hence they tend to take samples typically riper than the final crushed grape produces. Berry sampling is normally carried out with vines being sampled across a vineyard, taking into account topography and soil variations. Typically, a 100 berry sample is taken per hectare of vines with 2–3 berries being taken per vine. A total juice sample of approximately 300 berries is required to provide enough juice for analyzing sugar content, pH, titratable acidity and aroma and flavor assessment (Iland et al., 2000). The grape samples should be kept cool and the amount of berry damage minimized to avoid oxidation and subsequent change in the aroma and flavor characteristics. Bunch sampling (30 clusters per hectare) gives a reasonably representative sample whilst minimizing fruit damage. It has been noted that the between-vine variation is larger than the within-vine variation.

Crushing of the chilled fruit sample is carried out in the presence of 80 mg/l SO_2 and 60 mg/l ascorbic acid. Pectolytic enzymes are added at approximately twice the recommended rate (0.03 g/l) to ensure rapid clarification and the sample stored in the refrigerator in a sealed container (e.g. a capped 250 ml measuring cylinder). The clear juice is removed the following day and analyzed.

The assessment of aroma and flavor is crucial since flavor adjustment of the must is not an option available to the winemaker, although sugar and acidity adjustments are allowed in some countries. In cold climates, sugar is often a permissible adjustment, and in warm to hot climates acid addition is regularly practiced. The analysis of the development of flavor compounds suggests that peak fruit flavor does not necessarily occur at the optimum sugar-acid balance (Figure 5–1). From a winemaking point of view, the best composition of the must for dry white wine production would be at 21 Brix, 5.0 g/l acidity and pH 3.40. Beyond the second harvest point, 22.8 Brix, the juice pH begins to rise dramatically and the acidity drops to unacceptably low levels, both of which can be adjusted to some degree by acid addition.

Hence, however subjective the technique, the winemaker should try to qualify the flavor changes taking place in the vineyard using descriptors and, if possible, quantify differences using intensity ratings. It is helpful to add an additional 40 mg/l SO_2 to a sample and retain it for comparison with the following week's sample. Examples of some of the descriptive flavor changes in Chardonnay, Sauvignon Blanc and Riesling are given in Table 5–3.

The other factor governing fruit quality and harvesting decisions is the presence of mould or spoilage organisms. Damaged fruit may begin fermentation caused by wild yeast, or may become infected with *Acetobacter*. Infection of the grapes by moulds, particularly *Penicillium* and *Aspergillus*, has been shown to produce off-flavors in the wine (Nelson and Ough, 1966). A number of techniques have been developed for monitoring fruit condition including HPLC analysis (Kupina, 1984) and laccase determination using a colorimetric reaction with syringaldizine (Grassin and Dubourdieu, 1989). Laccase is a very active polyphenol oxidase enzyme

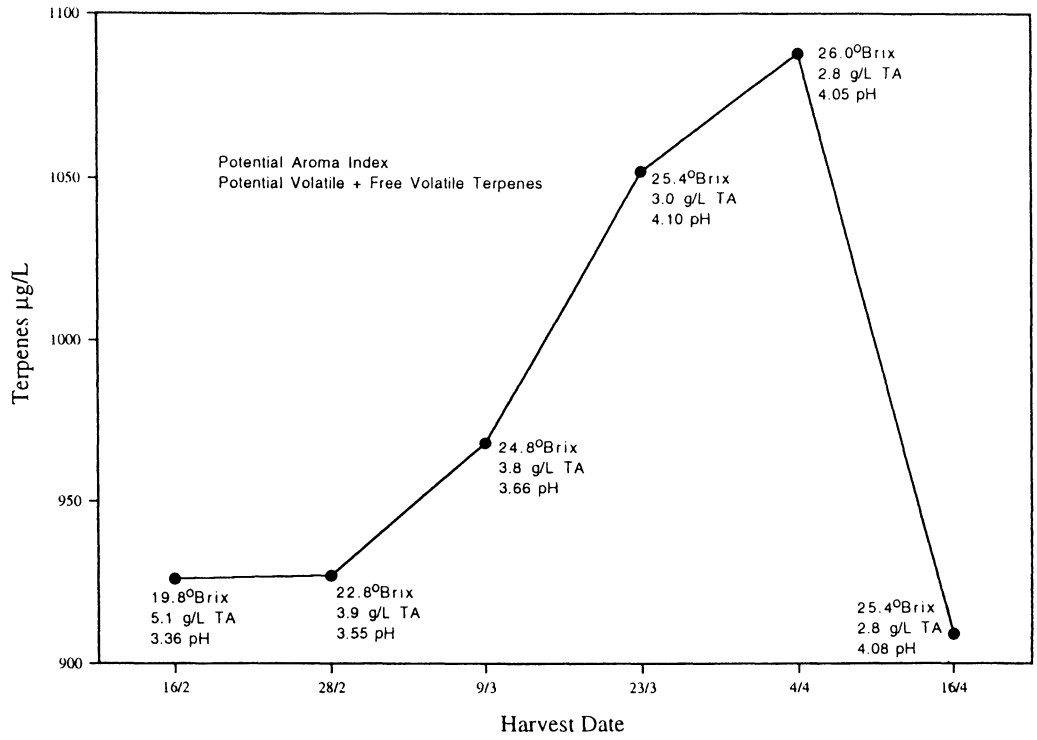


Figure 5–1 Total volatile terpenes in Muller Thurgau at six harvest dates, Barossa Valley, Australia, 1984.

which is produced primarily by the mould *Botrytis cinerea.* In white juice and wine it causes rapid browning.

Having determined the time of harvest, the winemaker must ensure that the fruit reaches the crusher with minimum deterioration in quality. Of primary concern is the control of oxidation and the inhibition of spoilage organisms. Both these factors are aggravated by high temperature and fruit breakdown. The avoidance of metal contamination by using precoated metal picking containers is an important quality factor. Harvesting the fruit cool, minimizing the amount of handling and reducing the time between picking and crushing all contribute to maintaining fruit quality (Table 5–4).

Table 5–3 Descriptive flavor changes during maturation of three varieties of white grape

	Riesling	Sauvignon Blanc	Chardonnay
Increasing	Green/unripe grapes	Green/unripe grapes	Green/unripe grapes
Fruit	Green/light floral	Light herbaceous-grassy	Cucumber
Maturity	Citrus-lime	Strong herbaceous	Cashew
↓	Broad floral	Capsicum	Tobacco
	Perfume floral	Tropical fruit	Melon
	Herbaceous		Ripe fig
	Tropical fruit		
	Muscat		

From Jordon and Croser (1983).

Table 5–4 The effect of delayed processing on the composition of Colombard juice

	Holding temperature 11°C			*Holding temperature 22 °C*		
	Brix	*pH*	*Titratable acidity*	*Brix*	*pH*	*Titratable acidity*
Control	23.17	3.25	8.9	23.17	3.25	8.9
Holding overnight	22.77*	3.26	8.0*	22.77*	3.28	8.0*
Holding 2 days	22.57*	3.48*	7.4*	22.57*	3.51*	8.1*

*Treatment differs significantly from control at $P < 0.05$.
Adapted from Marais (1977).

In warm to hot climates, night harvesting using mechanical harvesters has substantially reduced the fruit temperature on arrival at the winery. It is desirable that the fruit temperature is below 15 °C. With savings of between A$149/ha to A$1150/ha for mechnically harvesting Shiraz and Cabernet Sauvignon, respectively, the economic realities of the process are evident (Cook and Simes, 1985). Studies on the effect of mechanical harvesting on wine quality have generally shown no difference between hand harvesting and mechanically harvested fruit (Noble et al., 1975; Wagener, 1980). The even distribution of SO_2 (100 mg/kg as potassium metabisulphite powder) and ascorbic acid (80 mg/kg) to the harvesting bins has further led to the control of oxidation at the juice stage (Ewart et al., 1987). The level of SO_2 required is dependent on fruit maturity, temperature and environmental conditions (Table 5–5).

Whilst the adoption of anti-oxidant procedures is desirable for retaining fresh fruit characters in the resultant wines, the active introduction of oxygen to the must at the crusher is also practiced (Guerzoni et al., 1981; Piva and Arfelli, 1991). This 'active oxidation' (also known as 'hyperoxidation') results in depletion of polyphenol oxidase activity and the removal of the phenolic substrates by polymerization and precipitation (Table 5–6). The brown oxidation products produced in the juice (monitored at 420 nm) are substantially removed during the fermentation and the resultant wines, depleted of an oxidisable substrate, are stable against further oxidation. The loss of fresh fruit characters from this treatment may not be detrimental to full-bodied, full-flavored wines but does detract from the floral, fruity style wines.

The process of crushing is intended to remove the grapes from their stalks and to split open all the grapes to enable juice extraction. Commercial crushers either destem before passing the grapes through adjustable rollers or destem after crushing. The former is preferable as it mini-

Table 5–5 Sulphur dioxide additions to grape bins

	Sulphur dioxide additions at various fruit temperatures (mg/kg)		
Fruit pH	*Low (< 15 °C)*	*Moderate (15–25 °C)*	*High (> 25 °C)*
Low (< 3.3)	60	70	80
Moderate (3.3–3.7)	80	90	100
High (> 3.7)	100	110	120

Mouldy fruit will require sulphur dioxide additions of 150–180 mg/kg.
Since potassium metabisulphite (PMS) contains *ca.* 50 % of available sulphur dioxide, the figures given in the table should simply be doubled to obtain the amount of PMS to add.

Table 5–6 Effect of inhibition of must oxidation on juice phenolics and browning levels in juice and wine

Treatment	*Total Phenolics in juice (280 nm)*	*Browning (OD 420 nm)*	
		Juice	*Wine*
Control (must oxidation permitted)	1.7[a]	0.48[c]	0.08[c]
Carbon dioxide 150 g/kg fruit	1.5[a]	0.44[b]	0.08[c]
Sulphur dioxide 50 mg/kg fruit	2.9[b]	0.09[a]	0.07[b]
Sulphur dioxide 100 mg/kg fruit	3.6[c]	0.08[a]	0.06[a]
Sulphur dioxide 100 mg/kg fruit plus sodium erythorbate 50 mg/kg fruit	3.4[c]	0.08[a]	0.07[b]

Values with the same letter are not significantly different at the 5 % level.
From Ewart *et al.* (1987).

mizes the possibility of stems being ground in the rollers, thereby releasing bitter phenolics. Likewise, careful adjustment of the rollers is required to avoid crushing of the seeds. For floral, fruity wines, it is important to minimize phenolic extraction and oxidation.

Once crushed, the must is pumped to a drainer for the separation of the juice. If the fruit temperatures are much above 15 °C then an in-line must chiller may be used to reduce the temperature to 5–10 °C. Maximizing flavor is one of the key goals of the winemaker. Since most of the flavor compounds are located in the skin region, flavor extraction can be enhanced by leaving the juice in contact with the skins for periods of up to 12 hours (Figure 5–2). An undesirable aspect of this practice is an increase in the levels of phenolics extracted. Chilling the must reduces the degree of phenolic extraction and is an important quality control parameter. The fuller bodied wine styles can tolerate a higher degree of skin contact than the light delicate fruity-floral wines. The free run juice from the drainer or press is the lowest in phenolic material and is considered the best quality. One technique used to reduce phenolic levels is to whole bunch press the fruit. This is time consuming and results in lower free run juice yield but does produce superior quality juice. In a considerable number of wineries the press is used as the draining vessel with the must being pumped directly into it from the crusher.

Juice yield varies with variety and is usually in the range of 550–650 l/tonne of grapes for free run and an addition 50–100 l from pressing. This yield is also dependent on the type of press used and the pressures exerted. The free run and pressings juice are normally kept separate with the option of combining them postfermentation. Heavy pressings from a continuous screw press are usually only suitable for the production of distillation wines. During the transfer of the skins from the drainer to the press and after making the pressings cut in the case of the press being used as a drainer, an additional 100 mg/kg of SO_2 may be added.

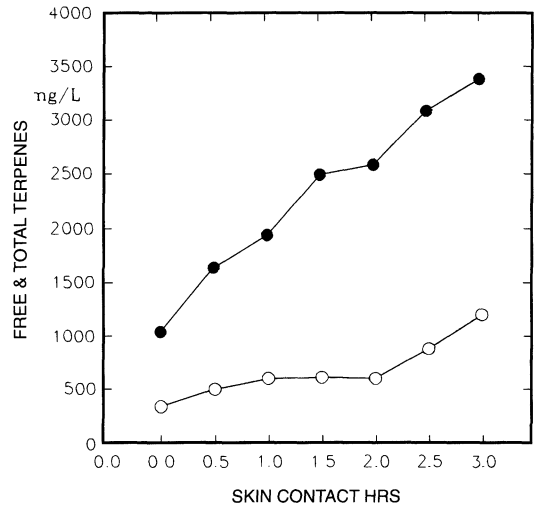


Figure 5–2 Free and total volatile terpenes for Eden Valley Traminer 11.6 Be, pH 3.2, titratable acid 7.5 g/l, 15 °C. ●, Total volatile terpenes; ○, free volatile terpenes (from Kluczko, 1985).

PREFERMENTATION TREATMENTS

Amelioration or adjustment of the must and clarification to remove solids are the two major considerations prior to fermentation. The adjustment of the must enables the winemaker to start the fermentation with all juice components in balance. In a warm to hot climate the juice is likely to require addition of acid, whilst in cool to cold climates sugar addition and deacidification may be required. Juices high in pH and low in titratable acid taste flat and unbalanced as well as being less stable to oxidation and microbial spoilage. Musts with low pH, whether naturally occurring or as a consequence of acid adjustment, require less SO_2 to control the native flora and to ensure the onset of a desired fermentation. This is because pH plays a major role in dictating the form of SO_2 present in the juice and hence its effectiveness in inhibiting microorganisms. Free SO_2 exists in ionized and molecular forms, the proportions of which are determined by pH (Figure 5–3). The molecular SO_2 is the form that is toxic to yeast. Sulphur dioxide bound to acetaldehyde or to other carbonyl compounds has little or no anti-microbial activity (Lea—this book). For juice with pH values below

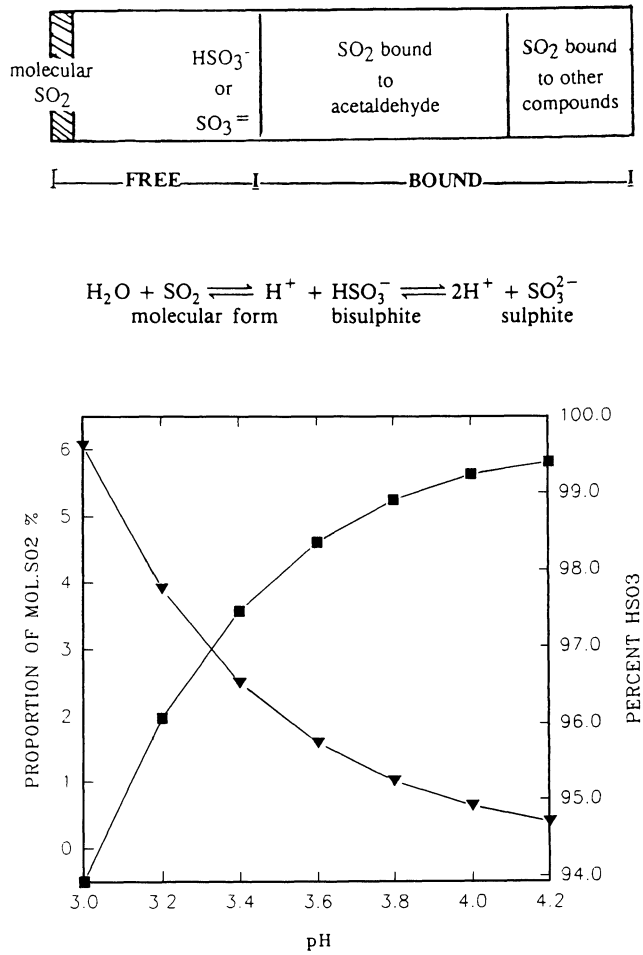


Figure 5–3 Forms of SO_2 in wine and the effect of pH on molecular SO_2 concentration in aqueous solution ▼, Molecular (mol.) SO_2; ■, Bisulphite (from Macris and Markakis, 1974).

3.3, where previous sulphite additions have not been made, SO_2 should be added at 60–80 mg/l. In the case of juices with pH values above 3.7, this should be increased to 100–120 mg/l.

The lowering of the pH prior to fermentation results in cleaner wines free from off-odors mainly because of the suppression of wild yeast and bacteria in the juice stage and the early dominance of the added yeast starter culture. The lowering of the pH must be constrained by the effects that the added acid has on the taste of the wine. The relationship between pH and titratable acidity is affected by the cations present in the juice, primarily potassium but also sodium. Once the grapes are crushed and the compartmentalized potassium is released, salts of tartaric acid (potassium hydrogen tartrate and dipotassium tartrate) can form. The extent of cation exchange is the sum of the cations present divided by the sum of tartaric and malic acid in the must. The extent of cation exchange (Boulton, 1990) means that juices high in potassium and/or sodium have high pH with high acidity, giving the winemaker less room for adjustment.

During fermentation, and postfermentation when carrying out cold stabilization, some of the tartaric acid will precipitate out as potassium hydrogen tartrate thus lowering the acidity. Depending on the pH of the wine at the time of stabilization, the final pH will either be lower or higher (Figure 5–4). In terms of pH reduction, it is advantageous for a winemaker to have the pH value of the wine below 3.56 prior to cold stabilization.

In the case of the high-acid musts, deacidification can be achieved using either calcium carbonate or the calcium 'double salt' precipitation of malic and tartaric acid (Mattick et al., 1980). The latter method is used on very high-acid musts in cool climates, where both malic and tartaric acid levels need to be reduced. The use of the specialized yeast *Schizosaccharomyces pombe*, which reduces malic acid levels during fermentation, has been generally unsuccessful because of the off-flavors and aromas which it produces (Rooyen and Tracey, 1987).

For mould-infected fruit, fining with bentonite and in severe cases with carbon prior to fermentation reduces off-odors and flavors, resulting in a cleaner ferment. It should be noted that carbon will also strip fruit flavors and needs to be used cautiously. Rates are typically 0.5–1.0 g/l depending on the degree of fruit mouldiness, although the fermentation itself will remove a certain amount of mouldy character. All fining rates should be assessed by laboratory trials. With a particular focus on low phenolics for the floral and fruity wines the use of light sodium caseinate/PVPP finings (20 to 80 ppm) is often practiced on the free run juice and racked prior to fermentation. For the pressings, higher rates of PVPP typically 200 to 800 ppm are required to strip the excess phenolics. The use of the combined sodium caseinate and PVPP fining results in better fruit flavor retention than using PVPP on its own at the same rates.

For the production of the 'floral-fruity' style, the removal of grape solids is essential. High grape solids result in the production of higher alcohols such as isobutanol, 'active' amyl alcohol and isoamyl alcohol (2- and 3-methyl pentanol, respectively) and a loss of the fruity ethyl esters and acetate (Singleton et al., 1975; Klingshirn et al., 1987). This process can be achieved by cold settling (natural gravitation) or by mechanical means such as filtration or centrifugation. For cold settling, refrigeration is required to cool the must to 5–8 °C, typically for 24 hours. Clarification can be aided by the addition of pectolytic enzymes. In some cases, fining agents such as bentonite or gelatin and kieselsol are used in place of enzymes. In general, a reduction of solids to below 0.5 % is satisfactory, although a number of winemakers advocate only fermenting 'filter bright' juice. In this case, stuck or difficult fermentations are often experienced unless the yeast is aerobically propagated and given nitrogen supplements and inert solids. The solids in juice provide a site for budding yeasts and for carbon dioxide and ethanol release, so preventing toxicity from the end products of metabolism. The addition of grape solids, diatomaceous earth or bentonite to such juices results in increased fermentation rates (Groat and Ough, 1978). More recent work with expanded cellulose fibres has proved to be effective in preventing stuck fermentations by providing budding sites for the yeast

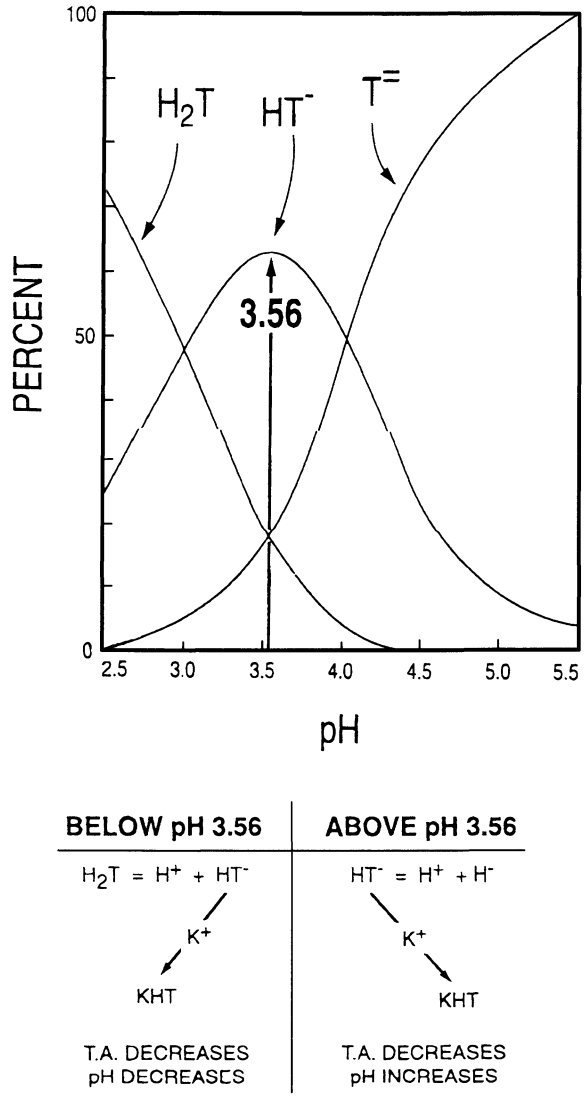


Figure 5–4 Tartrate equilibrium diagram and equilibrium between species of tartrate (from Iland, 1987).

with entrapped oxygen within the fibrils. The cellulose also absorbs yeast toxins thus reducing the chance of stuck fermentations.

YEAST AND FERMENTATION CONTROL

The winemaker's objective is to ensure a rapid onset of fermentation and for the fermentation to proceed steadily to completion or dryness. During this process, the aim is to retain the fruit characters of the grape, to enhance the production of yeast-derived fermentation esters and to avoid the production of off-odors such as hydrogen sulphide, mercaptans, ethyl acetate or acetic acid.

Effective control of the fermentation is achieved by early dominance of a selected yeast strain. Although such yeasts are classified generally as *Saccharomyces cerevisiae, S. uvarum* or

S. bayanus, considerable work carried out on yeast strain selection has resulted in a wide variety of yeasts which are available for conducting the fermentation (Kunkee, 1984; Rankine, 1968). The required characteristics are those of being a strong fermenter, not producing undesirable off-odors, efficiently converting sugar to ethanol and flocculating well. Different strains produce different balances of aromatic esters. This means that the winemaker is able to select a yeast which produces fruit-like esters and thus enhance wines in the floral-fruity styles. These fermentation esters are often short lived but do contribute to the fresh fruit wine style for early consumption. In the case of full-bodied, full-flavored wines, a more neutral yeast which impinges less on the varietal characteristics of the grape may be the yeast of choice.

Traditionally, yeast starter cultures have been built up from yeast slopes or from freeze-dried cultures. The step build-up is 20 times the volume at maximum cell count (1.6×10^8 cells/ml) in the presence of vitamins (such as thiamine and pantothenate) plus amino nitrogen supplements and air. This promotes rapid cell growth and the production of lipids and sterols, which are particularly important in ensuring that the fermentation of highly clarified juices goes to completion (Monk, 1982). There is now a large selection of active dried wine yeast available commercially which alleviates the need to build up a starter culture from a stored slant. One of the problems with yeast is the apparent high rate of mutation and the need to constantly re-evaluate and reselect strains.

Inoculation rates in white wines range from 3–5 % by volume using an actively fermenting starter culture with the objective of achieving a final cell count in the juice of 1×10^6 cells/ml. Highly clarified juices which have been processed and held under anaerobic conditions are often difficult to ferment to dryness. It is crucial that adequate starter culture preparation be undertaken. Under anaerobic conditions yeast do not produce sterols, which are essential for their metabolism and growth (Table 5–7). It is therefore important that the yeasts are aerated during the propagation phase, so that reserves of sterols can be built up which enable the yeast to complete the fermentation. In the case of dried yeast inoculations the use of proprietary yeast supplements, or diammonium phosphate plus cellulose fibres is recommended.

Control of the fermentation rate is managed by the use of refrigeration with temperatures being maintained in the 10–15 °C range. The objective is to maintain a steady fermentation rate (0.74 to 1 ° Baume/day) and reduce the loss of volatile esters which occurs at high fermentation temperatures. The fermentation temperature also has a direct effect on the nature of the higher alcohols formed during fermentation. Temperatures in the 10–15 °C range result in the production of fruity esters whilst temperatures around 20 °C produce the higher alcohols such as

Table 5–7 The influence of ergosterol, oleanolic and oleic acid on yeast fermentation after 48 hours in synthetic grape juice

	Aerobic fermentation		*Anaerobic fermentation*	
	Yeast (cells/ml × 10^6)	*Sugar fermented*	*Yeast (cells/ml × 10^6)*	*Sugar fermented*
Control	124	91	67	59
Ergosterol (86 mg/l)	—	—	74	58
Oleanolic acid (100 mg/l)	—	—	90	63
Oleic acid (20 mg/l)	—	—	66	63
Ergosterol + oleic acid	—	—	83	74
Oleanolic + oleic acid	—	—	197	89

From Ribéreau-Gayon *et al.*, 1975.

isoamyl alcohol and hexanol (Ough and Amerine, 1967).

The addition of the montmorillonite clay bentonite to the fermentation will facilitate an even fermentation of juice low in solids, will ensure rapid clarification at the end of fermentation and can achieve protein stability at lower levels of bentonite fining than with postfermentation additions (Ewart et al., 1980). Caution is required when adding bentonite to the ferment in order to achieve protein stability. It is important to add the bentonite during the first half of the fermentation. Additions at the start can delay the onset of fermentation by flocculating the yeast. Late additions require higher rates to achieve stability and may prematurely end the fermentation. Laboratory trials need to be conducted to establish the level of bentonite required to achieve protein stability. Since the alcohol formed during fermentation will denature and precipitate some of the proteins, trials determined on the juice will result in slightly overfining the wine. Bentonite fining during fermentation requires less bentonite to achieve protein stability than immediate postfermentation additions. This protein stability procedure is suitable for batch operations and has the added advantage of minimizing postfermentation handling and the potential for oxidation.

Where wines of differing composition are to be blended, protein stabilization should be carried out after blending has taken place since a change in wine pH may render some of the previously stable protein fractions unstable. Work by Waters (1991) has shown that with increased storage time the level of bentonite required to protein stabilize the wine decreases. Thus if the wine is to be held in storage for some time, as with barrel-aged Chardonnay, fining at the end of maturation is likely to result in lower levels of bentonite being required. The wood tannins will also aid in the precipitation of unstable protein.

Fermentation monitoring consists of daily checks of sugar (by hydrometer) and temperature. In addition, the wines should be tasted to check for the presence of undesirable odors or flavors. Musts which are low in free amino nitrogen are likely to produce hydrogen sulphide during fermentation caused by the proteolytic activity of yeast seeking a source of nitrogen and thereby degrading sulphur-containing amino acids (Vos and Gray, 1979). In such cases it is advisable to add 200 mg/l diammonium phosphate at the start of the fermentation and a further 100 mg/l during the fermentation if hydrogen sulphide is detected. Diammonium phosphate additions are only effective during fermentation. If hydrogen sulphide persists at the end of fermentation, treatment with SO_2 and mild aeration is recommended before resorting to the use of copper sulphate. Wine left untreated will result in the hydrogen sulphide forming the more stable ethyl or diethyl mercaptan which has a lower aroma threshold and hence is more readily detected. These mercaptans have onion or garlic type odors.

It is important for the winemaker to establish whether is is hydrogen sulphide or ethyl mercaptan present in the wine, since aeration will remove hydrogen sulphide but will cause ethyl mercaptan to form the more stable polymercaptan (diethyl mercaptan).

Laboratory trials should be conducted to establish which sulphide form is present. Cadmium sulphate removes hydrogen sulphide only, whereas copper sulphate removes hydrogen sulphide and ethyl mercaptan. Therefore with an untreated sample the winemaker can establish which form exists in the wine. If the sulphide odor disappears with cadmium and copper sulphate treatment, the problem is hydrogen sulphide. If it is removed by copper sulphate only, it is ethyl mercaptan and if it remains after copper treatment, it is diethyl mercaptan. The laboratory samples should be smelled only, as cadmium is toxic when ingested. Laboratory trials must be carried out to establish the minimum levels of copper required, since copper in excess of 0.5 mg/l can result in later instability problems and the formation of white 'copper casse'. Treatment of the wine with 0.2 to 1.5 mg/l of copper sulphate will remove hydrogen sulphide and ethyl mercaptan but the double sulphide bond in diethyl mercaptan has to be broken with ascorbic acid (50 mg/l) before treatment with copper.

Sources of hydrogen sulphide include vineyard spray residues, particularly elemental sulphur which is used to control powdery mildew on grapes. Work by Thomas *et al.* (1993) suggests that elemental sulphur additions to the must at rates typically found on the grapes is in the range of 0 to 3.4 mg/l and does not result in hydrogen sulphide production. This work also found that during fermentation hydrogen sulphide production peaked at two stages, i.e. between day 1 and day 2 and at the end of the fermentation. Yeast strains vary considerably in their ability to produce hydrogen sulphide, which is a metabolic intermediary in the production of cysteine and methionine (Eschenbruch, 1974). Thomas *et al.* (1993) found only the first peak was influenced by yeast strain and that the second peak, which is likely to lead to residual hydrogen sulphide in the wine, was affected primarily by the fermentation medium.

High juice solids also results in the production of volatile sulphur compounds (Lavigne *et al.*, 1992). Occurrences of hydrogen sulphide have been observed with clean wine after transfer into caustic-washed stainless steel tanks which previously contained fermenting sulphidic wine. This has pointed to manganese sulphide being the source. The manganese sulphide can form on the walls of the tank and becomes fixed during caustic washing. It is then only released in a subsequent acid wine medium. A citric acid rinse of the tank avoids the likelihood of this problem occurring.

Fermentation of white wines is preferably carried out in closed but vented vessels ranging from oak barrels to large stainless steel tanks. The floral, fruity wine styles are fermented in stainless steel, since the volatiles extrated from the wood mask the floral fruit attributes. However, wood characters enhance the complexity of the full-bodied styles which are either fermented in wood or aged in wood for a period as finished wine. The general view of winemakers is that fermentation in wood gives the best integration of fruit and wood, avoiding some of the sappy green characters which sometimes result when finished wine is aged in new poorly cured oak casks. The disadvantage of such a practice is that the effective life of the cask is reduced because of yeast deposits which clog up in the pores in the wood. Fermenting in the barrel is also more labor intensive as it requires partially filling the barrels and monitoring a large number of fermentations rather than just one or two tanks. Towards the end of the fermentation the barrels have to be topped back full.

Temperature control in oak casks is usually achieved by having the casks in a temperature-controlled room or cool underground cellar. However since wood is a fairly effective insulator real temperature control is difficult. Once the fermentation has begun to slow down, the temperature should be allowed to rise to 15–18 °C to facilitate the completion of fermentation. At this stage, the vessel should be topped up to minimize ullage (headspace) and all vessels less than 20 000 l should be fitted with airlocks to permit carbon dioxide out and to prevent air entering the headspace. Once two consecutive hydrometer readings are the same, a sample should be analyzed for reducing sugars. The wine is considered dry when the reducing sugar reaches 2.5 g/l or less.

POSTFERMENTATION OPERATIONS

Once dry, the clear wine is racked off gross lees to a carbon dioxide sparged tank, all hoses first being purged with inert gas before transferring the wine. Sulphur dioxide is added at 40–50 mg/l to provide a free SO_2 level of 20–25 mg/l which prevents oxidation. For the delicate fruity wine style, the addition of 30 mg/l ascorbic acid is often made as an additional anti-oxidant at each stage of handling or transfer; SO_2 is relatively slow at binding oxygen, whilst ascorbic acid is a rapid oxygen scavenger. The form in which SO_2 exists in wine is dependent on the wine pH (Figure 5–3). At low pH values the dissociation is towards molecular SO_2 which is more reactive and has strong anti-microbial activity, and hence the total SO_2 addition required to produce a free SO_2 of 20 mg/l is less than in wines of higher pH.

One of the reasons for racking the wine as soon as possible after the end of fermentation is to avoid the formation of hydrogen sulphide from the breakdown of yeast cells at the bottom of the tank. This autolysis releases sulphur-containing amino acids and, under the reductive conditions existing in the bottom of large tanks, hydrogen sulphide may form. Wine in large tanks can be kept on yeast less for up to 2 weeks but should be carefully monitored for the development of hydrogen sulphide and racked immediately if it is detected. Barrel fermentation, by comparison, often uses yeast autolysis as an added complexity factor in the production of full-bodied wines. Such wines may be left in contact with yeast lees for up to 12 months without the formation of hydrogen sulphide. The limited volume of the barrel and the way in which the yeast deposits around the walls of the cask means that there is not a great depth of yeast lees at any particular point. This, and the practice of resuspending the yeast lees once a week for up to 4 months, appears to prevent sulphide odors developing.

As no SO_2 is added to these barrel-fermented wines at the end of yeast fermentation, a secondary malo-lactic (bacterial) fermentation often takes place during extended lees contact. Inoculation of the wine with an active culture of malolactic bacteria is sometimes practiced and would usually take place after the final stages of primary fermentation. A range of malo-lactic bacteria strains are now available in a freeze-dried form which are grown up in sterile diluted grape juice prior to inoculation (Krieger, 1993). The malolactic fermentation can be monitored using paper or thin-layer chromatography to follow the disappearance of the malic acid and the enlargement of the lactic-succinic acid spots (Iland et al., 2000). More precise measurements of malic acid may be made using enzymatic or HPLC assays (Amerine and Ough, 1980). Typically Chardonnay wines will have a proportion of the blend up to 40 % having undergone a malo-lactic fermentation, depending on the degree of buttery-diacetyl character sought by the winemaker.

In cold climates, deacidification by means of malo-lactic fermentation is often required to make the wines palatable. Once the desired level of malolactic character has been achieved, SO_2 is added to inhibit further bacterial activity. During the malo-lactic fermentation, the wine is protected by the carbon dioxide which is released from the decarboxylation of malic to lactic acid. Once this process slows down, there is real danger of air entering the headspace resulting in oxidative browning and, in the absence of SO_2, the encouragement of *Acetobacter* growth.

Postfermentation should see the free SO_2 levels maintained at 20–25 mg/l and all vessels full. The introduction of variable capacity tanks has been a successful method of eliminating headspace in tanks. Otherwise if wine is to be stored in a partially filled tank, the headspace must be filled with inert gas. Carbon dioxide is the gas of choice as it is heavier than air and forms a blanket over the wine. However, high levels of dissolved carbon dioxide are undesirable in still wines and, if gas blanketing is required during the later stages of processing, nitrogen or a 70 % nitrogen 30 % carbon dioxide mix is preferred. Recent trials have successfully used argon and argon/CO_2 as an inert gas for blanketing wine. Argon has the advantage of being heavier than air and is not soluble in the wine. The disadvantage is the cost.

Wine blending, where required, should be carried out prior to protein and tartrate stabilization. Heat sensitive grape proteins have the ability to denature in the bottle and cause clouding. These proteins are removed by the use of bentonite, which is added to the wine as a fining agent at rates of 0.2 to 3.0 g/l. There are numerous tests used worldwide to determine the protein stability of wine samples. These tests generally use heat, strong acid, tannin, ammonium sulphate or a combination of these. The most reliable appears to be heating the bentonite-fined and filtered sample at 80 °C for 6 hours. After cooling to room temperature, the samples are examined by holding up to a bright light. The bentonite fining level that produces no haze is then chosen for fining the tank of wine.

Wines that have been fermented in contact with bentonite should be checked to ensure they

are protein stable. Protein haze in wine is not only caused by thermolabile proteins but can also be the result of protein-tannin-metal complexes. Recent work has shown that polysaccharide fractions present in wine confer a degree of protein stability and may offer an alternative means of achieving protein stability in white wines (Waters, 1991). Bentonite fining to remove protein has two disadvantages: one is the large volume of lees (insoluble solids) formed at the bottom of the tank and the other is the degree of flavor stripping that takes place (Simpson, 1979; Ewart et al., 1980).

Tartrate stabilization is the removal from the wine of excess potassium hydrogen tartrate and calcium tartrate which may cause a crystalline deposit in the bottom of the bottled wine. Whilst these deposits are not harmful and the wine can readily be decanted, their presence is regarded by most consumers as being a defect. The standard procedure for stabilizing wines is to hold them just above their freezing point for 7 to 14 days. This results in a decrease in the solubility of potassium hydrogen tartrate and to a lesser degree that of the calcium tartrate, resulting in precipitation (Berg and Keefer, 1958; Berg and Akiyoshi, 1971). This process can be speeded up by seeding the wine with potassium hydrogen tartrate crystals which serve as nuclei for crystal growth thus eliminating the crystal induction phase.

The 'contact process' for cold stabilization uses very high seeding rates of potassium bitartrate (4–6 g/l) and achieves stabilization within 60–90 minutes (Rhein and Neradt, 1979). The wines are filtered cold to remove tartrate crystals still in suspension. Care must be taken to avoid oxygen pickup during the handling of the cold wine since oxygen is very soluble at low temperatures. All hose lines should be purged with gas and all pump seals and hose fittings checked. Alternative methods of tartrate stabilization include ion exchange to remove potassium ions, electrodialysis (Postel and Prasch, 1977), reverse osmosis and the addition of crystal inhibitors such as meta-tartaric acid and carboxymethyl cellulose.

Cold stability tests vary from the determination of the concentration product as a measure of potential solubility (Berg and Keefer, 1958), to holding a sample of wine at -2 °C for 7 days and observing if crystals form. One of the most reliable and simple tests is to monitor the change in conductivity of a sample after the addition of 1 g/l of potassium hydrogen tartrate. A change of greater than 5 % in the conductivity indicates that the wine is unstable and will need further cold stabilization.

Oxidative stability is the third area of concern to the winemaker. White wines are particularly sensitive to oxidation because of their low phenolic pool, and the results of oxidation are readily apparent against the pale background color. In order to increase the shelf-life and acceptability of the product, the winemaker needs to ensure that no undesirable oxidative changes will take place once the wine is in the bottle. The argument for the oxidative treatment of the must (see section 3) means that the phenolics which are susceptible to oxidative browning have already been precipitated, hence the wine postfermentation is no longer susceptible to further browning reactions.

Dissolved oxygen in the wine should be removed or reduced to below 0.5 ppm by sparging with nitrogen before bottling. Wines which still show a strong propensity to brown may be treated with a phenolic-removing agent such as polyvinylpolypyrollidone (PVPP). However, it should be noted that these agents will often strip the wine of aroma and flavor. A less stringent fining agent, which is also good at removing excess brown color, is casein, a milk protein fraction which denatures in the acid medium of wine causing a floc to form. The floc precipitates carrying the brown phenolic pigment with it. Removal is then achieved by racking and filtration.

Clarification of white wines using fining agents is achieved through the use of bentonite, or by gelatin plus kieselsol (an aqueous colloidal silica). The latter technique forms a floc *in situ* in the wine, which brings down suspended material as it settles. Mechanical clarification is carried out by centrifugation, earth or pad filtration. Most wines

will require a degree of filtration prior to bottling. With suitable fining agents and for a dry wine this may only be a polish filtration (where particles are removed down to 5μm), but some wines may require a three stage filtration and a final membrane filtration (0.45–1.2 μm) to remove bacteria and yeast. The last is particularly important for wines with residual sugar, to ensure that no further fermentation takes place in the bottle. During the final processing and bottling of the wine, contact with air should be minimized and the free SO_2 levels maintained at 25–30 mg/l. To minimize oxygen pick up during filling, the bottles should be purged with inert gas prior to and after filling.

The production of medium-dry white table wines is similar to that previously outlined, except that the finished wine retains fermentable sugar and hence additional precautions need to be undertaken to avoid refermentation. The most desirable way to achieve residual sugar is to stop the fermentation using refrigeration and to sterile filter once the required sugar level is reached. The alternatives involve the back blending of a dry wine with grape juice concentrate of approximately 60 ° Brix or preserved grape juice (20–25 ° Brix). The juice is either sterile filtered and stored under nitrogen, ion-exchanged to pH 2.5 and held at 65 mg/l free SO_2, or is ion-exchanged to pH 3.0 with 1500 mg/l total SO_2 added. This high sulphured juice is desulphured prior to use by way of the Brimstone process (Potter, 1979). The last two storage methods result in considerable flavor loss.

Sweet white table wines are produced from high-sugar grapes. The sugar concentration in the grapes is achieved as a result of infection by *Botrytis cinerea*, dehydration on the vine or on racks after harvest and freezing of the bunches (Eiswein). Wines produced from *Botrytis*-infected grapes are the most complex and balanced since the *Botrytis* metabolizes some of the organic acids. As the berry contents are concentrated as a result of the increased permeability of the epidermal cells, the final level of organic acids remain about the same as that prior to infection (Ribereau-Gayon et al., 1980). Simple drying to achieve dehydration of the berries concentrates both sugar and acid and results in a high-sugar, high-acid must.

Fermentation of botrytized must is difficult because of the high sugar (35 ° Brix) and low nitrogen levels and the presence of a yeast inhibitor produced by the *Botrytis*. The grapes are dehydrated and juice extraction is difficult. Skin contact for 24 hours facilitates juice extraction but also increases the extraction of the polysaccharide ß-glucan which results in extreme difficulty when filtering the wines. Laccase is very active in botrytized must and SO_2 additions of 150 mg/l are common in order to inhibit it. As SO_2 becomes rapidly bound in these wines because of the generation of carbonyl compounds by the mould, it is advisable to add 0.5 mg/l thiamin to reduce the level of pyruvic acid formed during fermentation. This reduces the overall sulphite-binding capacity. The addition of diammonium phosphate (200 mg/l) and the use of a selected yeast strain which can cope with the high osmotic pressure and will produce low levels of volatile acidity is desirable (Creed et al., 1988). Because the yeast is fermenting under high stress conditions, these wines are typically very high in volatile acidity and often approach 1.5 g/l. This, however, is part of the wine style.

Once the desired alcohol level has been achieved, the wine is clarified and SO_2 is added to give a free SO_2 concentration of 25 mg/l. These wines are relatively stable and are unlikely to undergo refermentation. This is not the case with wines made from partially dried fruit either from using the 'cut cane' technique (Meyer, 1969) or from harvesting the fruit and drying it on racks. Wines made from such fruit need to be stopped at the appropriate alcohol level, clarified, cold stabilized and sterile filtered into bottle with or without the addition of yeast inhibitors such as sorbic acid or dimethyl pyrocarbonate (DMPC).

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6

Red Wines

Roger Boulton

STYLES OF RED TABLE WINES

The composition of a wine is determined by the initial composition of the grapes and subsequently influenced by the cumulative effects of the particular reactions that it undergoes during the winemaking sequence. The combination of these effects, the grape cultivar and composition at harvest, pre-fermentation handling, fermentation conditions, microbial activity, barrel aging and other actions constitute the 'style' in which the wine is made. Red wine styles can range from the methodical, traditional ones to proactive and adaptive ones, with yet others being some combination of the two. In some wine styles, the effects of one or more of the aspects of the style (such as tannin extraction from seeds during fermentation or oak component extraction from the barrel during aging) can dominate the flavor, color or aging potential of the wine rather than being in balance. In other wine styles, more subtle contributions of several aspects are sought (by deliberately controlling conditions and in some instances minimizing them) in an attempt to make those of the grape flavor of central importance and the wine enjoyable to drink when young.

The vineyard site, the choice of cultivar and the cultivation of the vine will predetermine the potential for flavor and aroma components, while it is the growing conditions of the season that will determine the actual concentrations of these components that are available to the winemaker. In varietal wine styles this is of major importance and the subsequent winemaking actions will generally be aimed at maximizing the extraction and recovery of these fruit characteristics.

The effect of cool growing conditions on the development of certain distinctive components such as the pyrazines of Cabernet Sauvignon (and the white cultivar, Sauvignon blanc) has been recognized since the 1970s. It is thought that these findings also hold for Merlot, Cabernet Franc and related cultivars. While the methoxypyrazines have been shown to contribute much of this character in Cabernet Sauvignon and Sauvignon blanc (Bayonove et al., 1975) there are no such distinguishing components yet identified for most other red wine grapes of commercial importance throughout the world, such as Syrah, Pinot noir, Durif, Zinfandel, Barbera, Carignan, Sangiovese, Tempranillo, Gamay or Grenache.

In the case of the pyrazines in Cabernet Sauvignon, there are some winemakers and writers who believe that these are characteristic, desirable components and indicators of appropriate growing conditions, while there are others who consider them to be a defect caused by unsuitable circumstances and to be avoided at all costs. In other cultivars, the characteristics may be compounds that are not of sensory importance in the young wine but rather are the precursors of aroma developments that will follow as the wine ages either in the barrel or in the bottle.

The extent to which the fruit composition contributes to the wine also depends on the nature and extent of extraction and the chemical changes that can accompany the subsequent treatments and conditions to which it will be exposed. These treatments begin with the nature of the juice, skin and seed contacting prior to, during and after the ethanol fermentation. They include the practice of allowing a cool maceration before the yeast fermentation and that of extended maceration following it, as well as the distinctive alternative of carbonic maceration. The impact of the aging conditions varies with the cooperage type, the source and age of the wood, the contact time that is permitted and, to a lesser extent, the temperature, humidity and their diurnal variation, during the aging period. The point of induction of the malo-lactic fermentation and the subsequent sulphur dioxide regimen employed will have significant effects on the extent to which microbial tones are a factor in the wine. The polymerization of pigments and certain aspects of oxidation in the finished wine are also related to the way in which the wine has been handled after fermentation and during aging.

In recent years there has been a disturbing trend in which a number of wine writers and reviewers have confused oak aroma with wine quality, and the natural response by many winemakers is to pursue heavily oaked styles in order to have their wines favourably appraised. This is, however, leading towards a single, oak-aged style for most red wines that threatens to dampen out the natural variations resulting from varietal, seasonal and regional characteristics. It is these natural variations and the individual manipulations of them during winemaking that provide the diversity that can be found within any particular wine style. Similarly, it is the diverse range of flavors that exist within the red grape cultivars in commercial production that has enabled a wide spectrum of distinctive red wine styles to exist.

GRAPE MATURITY AND HARVESTING

In some regions, the decision to harvest is often controlled by the prevailing weather conditions or the availability of labor to pick the grapes, while in others it is often a conscious choice based on the sugar content and, less commonly, features such as the phenolic composition, color, flavor or acidity measures.

The cultivars differ in their individual phenology and this will determine the timing of developmental stages in a given growing region. In typical ripening, the accumulation of sugar (on a per berry basis) follows a sigmoidal curve being slow at the beginning, increasing to the fastest rate at intermediate sugar contents and then slowing as the final level is approached. The formation of phenolic components in the skins, including the pigments, is delayed until the moderate sugar levels are reached within the berry and the berry cells begin to soften and expand, at the point of veraison. They accumulate quickly and then level off at a maximum level, sometimes declining slightly as the sugar accumulation is completed. At the point of veraison, the level of malic acid declines because of respiratory activity while that of tartaric acid remains nearly constant. The loss of acidity and the uptake of potassium cause the titratable acidity to fall and the pH to rise during this period. While these changes generally occur on a per berry basis, there are variations in the actual concentrations because of changes in berry volume throughout the season and secondary variations on a diurnal basis. The volume of the berry varies with the cube of its diameter and small variations in berry diameter can lead to significant changes in component concentrations.

The development of flavors and aromas that are typical of the cultivar can follow a number of different patterns depending on the cultivar in question, differences in composition between the pulp and the skin and the prevailing growing conditions. The absolute levels are known to be influenced by a number of factors ranging from flowering, seed number and berry size and these in turn by vine age, growing conditions and sunlight exposure, with perhaps other contributions from factors such as root temperature, vine water status, cropping level and vine vigour. The patterns of flavor change in most red cultivars are not well understood as yet. This is complicated by significant variations between the vines within a vineyard, vineyard to vineyard variation in the nature and intensity of the flavor characteristics and it is sometimes compounded by differences of opinion as to which components are responsible for varietal character.

The development of the distinctive flavor components is thought to be independent of the biosynthesis of phenolics and color. The existence of darkly colored or highly tannic wines that have only low levels of distinctive aromas or flavors is a demonstration of this. In new regions, there will need to be a trial and error approach to determining the optimal maturity and, as in most regions, this will commonly be measured by the sugar content. The use of sugar content is merely an easily measured indicator of berry development rather than one that is strongly tied to other more significant components of berry composition. There is a critical assumption in such an approach that the development of desirable components always occurs in the same way with respect to the sugar content.

With the understanding that only about one third of the color and tannin of the grape will be released into the wine and that different contributions are made by the skins, seeds and stems to wine composition, it is not difficult to see that factors such as seed number, berry volume and skin area per unit volume are often as important as the concentrations of tannin and color in the berry.

The method of harvesting has less to do with the release of berry components from red grapes than it does for grapes to be used for the production of white and blush wines. The particular case in which carbonic maceration is employed requires that unbroken berries be delivered to the winery and as such the use of mechanical harvesting and deep grape bins would be excluded. In general, there is little evidence that mechanically harvested grapes result in significantly different wines and it is now widely used for harvesting in vineyards that can accommodate it.

PREFERMENTATION OPTIONS

The delivery of grapes to the winery is often the first point at which the winemaker can begin to influence the compositional aspects of wine. The grape cultivar will sometimes determine the kind of handling to be used, that is broken berry versus carbonic maceration. While the traditional application of the carbonic approach has been used with the Rhone cultivars (Pinot noir, Gamay, Carignan, Grenache, Syrah and Durif), winemakers outside of Europe have also used this approach with varying success and acceptance with Cabernet Sauvignon, Zinfandel and other cultivars.

The widespread practice of cluster handling is the breaking of berries and destemming of grape clusters to provide a must that will form the medium for the yeast fermentation. The grapes are generally removed from the stems and the berries crushed to form the must. The must is generally transferred to a fermentor by a positive displacement pump (a progressive cavity or rotary vane type). There have been advances in the design and selection of crushing equipment that have emphasized berry breakage and must transfer to provide a minimum of solids generation.

The fresh must may be cooled in a must cooler (either a shell and tube or spiral heat exchanger) and the skins may be steeped in the juice for a day or more prior to yeast inoculation. Damaged, machine-harvested and mold-infected fruit will often be treated with the addition of sulphur dioxide to levels of 50 to 75 mg/L to inhibit natural oxidases and to prevent spontaneous fer-

mentation by natural yeasts. Clean and cool musts will often be treated with additions of 50 mg/L sulphur dioxide or less to prevent the development of natural yeast and bacterial populations as the trend towards no addition at this stage has led to an increase in unwanted bacterial populations in many young wines.

The variations to this approach involve the partial crushing of clusters, destemming and the transfer of some whole berries into the fermentor along with the must and the less common practice of retaining a fraction or all of the stems in the must. The extent to which whole berries are included can vary from 10 to 50 % but typically is in the region of 15 to 20 % when this approach is employed. The practice of stem retention varies with the condition of the stems, which can show wide seasonal variation, and is generally less than 50 % when used. The stems can cause significant color loss because of anthocyanin adsorption, but they also contribute to the tannin extraction and provide a different phenol fraction from that generally contributed by the skins and seeds. The dry woody stems of some cultivars can contribute herbaceous aromas to the wine, but in general the stems are considered to be of either little value or a negative influence.

A contrasting approach is the use of carbonic maceration in which crushing is minimized or avoided entirely. Instead, the clusters are placed inside the fermentor, either stacked in trays or bins or dumped in with a minimum of breakage. (An alternative is the use of 1 or 2 tonne picking bins or plastic containers that can be covered but which facilitate the dumping and pressing of the berries after the treatment.) The fermentor is gassed with carbon dioxide to displace the air (and its oxygen) and an internal metabolism of the sugar and other metabolites by the grapes' natural enzymes begins. This respiration is not immediate and can take several days before it begins. Its activity and progression are usually monitored by the bubbling rate of the vented gas as it passes through a cup or cylinder containing a sulphite (or ethanol) solution. After a period of time (usually 3 to 4 days), the carbon dioxide begins to arrest the enzyme activity and the cellular respiration ceases. At this point, the clusters are transferred into the press and the expressed liquid is usually inoculated and allowed to ferment the remaining sugar in much the same way as a white wine would be handled. The wine is lighter in color and phenolic extraction than those made in the traditional, crushed-berry contacting method and it possesses characteristic aromas resulting from the treatment. The method requires hand-picked clusters that are free of mold and the facilities to hold the grapes at temperatures of 20 to 25 °C for several days.

In certain locations and in some seasons, the lack of color or the presence of mold requires that heat be used to enhance the extraction from skins and the inactivation of mold-derived enzymes. This treatment, known as thermovinification, is applied to the skins prior to fermentation and the fermentation is then conducted in the absence of the skins or seeds. In practice, the clusters are crushed and the must transferred to a tank from which a fraction of the juice is drawn, heated to a temperature of 45 to 55 °C and then pumped over the skins either continuously or periodically to obtain the desired extraction. The temperature employed, the treatment time and the skin and juice contacting, all contribute to the extent of extraction. Such juices are generally intensely colored but can easily be over-extracted with respect to tannin. Much of the additional color will be lost during the fermentation or shortly afterwards, although significantly higher tannin levels usually remain. The wines are usually fermented before the composition is modified by the adsorptive (fining) treatments. The use of temperatures above 60 °C leads to a more complete but usually unacceptable level of phenol extraction although such conditions are used in pigment-recovery processes.

JUICE, SKIN AND SEED CONTACTING

Of the phenols that are found in the seed and skins of grapes, less than half will be available for extraction into the wine. The proportion of the anthocyanins and flavonoid phenols that are

released into the wine varies between 20 and 40 % depending on the cultivar and vineyard location. Cabernet Sauvignon grapes can contain an estimated 1.4 mg of anthocyanins and 4.3 mg of phenols per g of fresh berries yet only 27 to 28 % of these can be found in the resultant wines (Van Balen, 1984). Similar variations have also been reported with Pinot Noir (Siegrist, 1985).

The contacting method employed will have a significant effect on the rate and a lesser effect on the extent of extraction, and a winemaker may adopt a particular contacting approach based on previous experience with the grapes to be used. Within each of the following contacting approaches there are nuances that can be introduced in an attempt to either enhance or diminish the natural variations in composition between the cultivars, but fine control is prevented since the composition is generally not known before the extraction occurs.

The study of color and phenol extraction in small-scale research fermentations is hampered by the lack of dynamic similarity in the temperature profiles when compared to the corresponding full-scale fermentations. This has long been recognized by researchers, but it is quantitatively demonstrated in the study by Scudamore-Smith et al. (1990). As a result, it is particularly difficult to perform small-scale extraction studies to compare such factors as vine manipulations, clonal differences and contacting methods, especially when quantitative analyses and sensory attributes are sought. The benefits and limitations of alternative contacting methods are often based on theoretical considerations or a limited number of empirical observations that have within them considerable variation caused by the cultivar, vineyard conditions, growing season and the individuals making the assessments.

Maceration Prior to Fermentation

In this approach the skins and seeds are permitted to soak for a period of 1 to 2 days prior to the initiation of the fermentation in an attempt to get a more aqueous extraction without the effects of ethanol on the grape cells. The must is generally cooled to between 15 and 20 °C to slow the onset of a natural fermentation and is usually pumped over once or twice each day to enhance the extraction. A heavily colored juice is obtained within 24 hours but the skins are retained and the mixture is inoculated. The fermentation usually proceeds slowly at first until the temperature rises to 25 °C or higher within 2 days. While this approach is practiced by a number of wineries, there are few analytical studies comparing either young or aged wines obtained by the method to those made by conventional contacting. This approach is alternatively referred to as 'cold maceration' or 'cold soaking'. While there have been a number of commercial trials of the influence of this extraction approach on the color extraction, the retention of color and the development of such wines during subsequent aging needs to be more thoroughly investigated.

Conventional Maceration

The conventional approach to must contacting is to transfer the new must into a fermentor, to inoculate with yeast (and if desired, malo-lactic bacteria) and to control the temperature in the range 25 to 30 °C. Within the first day of active fermentation, the skins will rise to the top of the juice and form a skin 'cap' that usually occupies about one third of the fermenting volume. Throughout the fermentation period, usually twice each day, juice will be drawn from the fermentor and pumped up to the top of the fermentor and distributed over the skin cap. This 'pump-over' operation usually provides a predetermined juice volume to the cap that will permeate the cap, displacing interstitial juice and partly lower the cap temperature. The setup used for the pump-over operation varies from simple discharge of a transfer hose into the headspace above the skin cap to rotating sprinkler devices suspended from the door in the roof.

The most common practice uses one juice volume during each pump-over operation and two such operations per day. Some wineries use two volumes per pump-over while others vary the volume and frequency, often beginning with

larger volumes or more frequent pump-overs in the early stages of fermentation and then reducing this towards the point of pressing. In larger fermentors, the cooling of the juice by external heat exchangers is generally incorporated into the pump-over operation.

An alternative to this approach is the draining the wine from the skins and seeds and transferring it to a second tank. The wine is then returned to the first tank, usually by splashing over the skin cap. This procedure is variously referred to as "de la stage" or "rack and return". It appears to provide a more complete mixing of the stratified volume than would usually occur by the pump-over operation, but there is little evidence that this results in any significant difference in color or tannin extraction. The method would allow for alteration of the relative amount of seeds to skins to be modified during the fermentation and that distinguishes it from other approaches.

The use of rolling, cylindrical, fermenting vessels, sometimes referred to as rotary fermentors (Peyron and Feuillat, 1985), has found limited acceptance. While the mixing of the skins and juice can be more extensive, there is little evidence that this results in more extensive or more suitable extraction, as is sometimes claimed. The fermentors are restricted to relatively small volumes because of limitations in heat removal, they are relatively more expensive to install and are not suitable for use as storage vessels.

The skins are especially rich in potassium compared to the fleshy part of the grape and this can effect changes in titratable acidity and pH by altering the extent of neutralization of the acid buffer as potassium extraction takes place. The potassium concentration generally increases slightly during the first days of fermentation then commonly falls towards the later stages of the fermentation (Van Balen, 1984). The potassium decrease in later fermentation is attributed to the spontaneous precipitation of potassium bitartrate (which is less soluble in the presence of ethanol) and this can contribute to the pH and titratable acid changes observed during fermentation. While the titratable acidity will always fall because of the precipitation of potassium bitartrate, the pH can fall, remain the same or rise , depending on whether the initial value is below, at or above approximately 3.8 and whether tartaric acid dominates the buffer capacity of the juice.

Maceration After the Fermentation

The practice of additional maceration following the completion of the fermentation has traditionally been used in some regions of Europe. The approach is claimed to provide additional extraction from the skins, which modifies the mouth feel of the young wine. Once the fermentation has finished, the fermentor is closed and left alone for between 1 and 3 weeks. When the gas bubbles which provide the buoyancy of the skin cap have left, it typically submerges and the skins fall to the base of the fermentor and are completely submerged. Studies of conventional extractions indicate that the peak in color occurs within the second day of fermentation (Ribereau-Gayon, 1974; Somers and Evans, 1979; Van Balen, 1984) while the total phenols usually show complete extraction by the end of the fermentation, typically after 5 or 6 days (Van Balen, 1984). It is doubtful that further extraction from the skins can take place if effective mixing and contacting has been provided during the fermentation. The more likely event is the continued extraction from the seeds which have usually only provided about 70 to 80 % of their extractable pool by the end of a 5- or 6-day fermentation. Studies of the extended maceration practice at wineries in California, primarily with Cabernet Sauvignon and Merlot grapes, have generally shown insignificant differences in pigment composition, or polymerization rates resulting from this treatment and the only effects are due to increases in the tannin content. The treatment is sometimes claimed to enhance the polymerization of pigment and the seed tannins but there is little evidence that this is actually occurring.

Carbonic Maceration

An alternative method, in which the extraction for the grape is quite different to that of conven-

tional contacting, is carbonic maceration. In this approach, the intact berries are surrounded with a carbon dioxide atmosphere and allowed to respire and to have partial fermentation by the grapes' own glycolytic enzymes. Some winemakers add a small volume of fermenting juice to the fermentor to provide the carbon dioxide for the atmosphere. The onset of the transformation generally takes place after several days at a preferred temperature of 35 °C and is usually detected by gas generation. There is a vacuum developed initially, then gas evolution during the metabolic phase and finally cessation of gas production when the fermentation has finished.

In the process, the cell walls in the skin become permeable allowing the pigments, many of the phenols and other extractables to leak into the intracellular fluid. After 8 to 10 days of berry fermentation, the enzymes lose their activity and the process ceases. The clusters are then transferred into a press and the berries are broken to yield their colored, partially fermented juice containing 1 to 1.5 % ethanol by volume. This juice is then inoculated and fermented to completion at temperatures of 15 to 20 °C, without the skins.

The wines produced in this way are usually lower in tannin with a distinctive aroma contribution in addition to the fruit character. The levels of varietal character are diminished and the value of this is debatable. The main chemical changes are the degradation of almost half of the malic acid, consumption of ammonia and the formation of the amide amino acids and succinic, fumaric and shikimic acids. A comprehensive monograph covering most of the current understanding of this process has recently been published (Flanzy et al., 1987).

The aroma produced by this procedure is quite distinct and Ducruet (1984) found four major volatile components that were present in significantly higher concentrations in wines made in this way. The components were benzaldehyde, ethyl salicylate, vinylbenzene and ethyl-9-decenoate; the formation of the first three is attributed to their involvement in the shikimic acid pathway.

While the traditional procedure employs carbon dioxide, the sugar conversion can be extended, almost to completion, by the use of nitrogen instead of carbon dioxide. It appears that it is the gas phase concentration of carbon dioxide that leads to a loss of enzyme activity (V. L. Singleton, personal communication). This would appear to provide possible variations from the traditional procedure that might be investigated further.

Color and Component Extraction During Conventional Maceration

The extraction of the color, tannins and other components from the skins and seeds during the fermentation shows a pattern which depends on the group involved. The following analysis attempts to quantify the rates and modes of extraction for the major groups so that strategies aimed at more selective extraction can be developed. In some cases, such as for the anthocyanin pigments, a partitioning equilibrium is established between the skin cells and the wine in the first few days, beyond which further extraction cannot be attained. By comparison, the tannin extracted from the seeds displays a two phase extraction that can continue for several weeks.

The chemical components responsible for the red and purple colors of red wines are the anthocyanins and these are found only in the outer layers of the skin of red wine grapes. In Vitis vinifera cultivars these include malvidin, peonidin, petunidin, cyanidin and delphinidin, primarily as their 3-glucosides (Singleton, 1988). The glucosides often have a smaller fraction acylated with acetic acid or one of the cinnamic acids. Table 6–1 shows the distribution within the pigments of young Cabernet Sauvignon and Merlot wines (Nagel and Wulf, 1979). One notable exception to the presence of acylated pigments in V. vinifera grapes is the cultivar Pinot noir. The anthocyanin patterns of other cultivars have recently been quantified using HPLC techniques (Port wine cultivars: Bakker and Timberlake, 1985; Syrah: Roggero et al., 1984; Tempranillo: Hebrero et al., 1988; several cultivars: Lay and Dreager, 1991).

The procyanidins are polymers of the flavan-3-ols that are between two and eight units in size.

Table 6–1 Pigment distribution in a young Cabernet Sauvignon wine

Anthocyanin	*Concentration (mg/l)*	*Percentage of total*
Delphinidin glucoside	49.4	12.9
Cyanidin glucoside	2.8	0.7
Petunidin glucoside	30.5	8.0
Peonidin glucoside	12.9	3.4
Malvidin glucoside	144.8	37.9
Malvidin glucoside acetate	77.0	20.2
Malvidin glucoside *p*-coumarate	15.8	4.1
Other acetates	41.4	10.8
Other cinnamates	7.5	2.0
Total	382.1	100

Source: Nagel & Wulf 1979.

They represent the major fraction within the polymeric phenols or 'tannin' and their special status results from their role in the polymerization of the anthocyanins during the first years in the life of a red wine.

In recent years, there have been a number of important studies that have quantified the dimer and, more recently, trimer procyanidin fractions of several red wine cultivars (Ricardo da Silva, 1990). The four main dimers, generally referred to as B1, B2, B3 and B4, have been quantified by HPLC for Cabernet Sauvignon, Merlot and Malbec (Salagoity-Auguste and Bertrand, 1984) and for Carignan and Mourvedre (Ricardo da Silva et al., 1992). Other studies have analyzed their levels in wines from different cultivars and regions (Etievant et al., 1988), their extraction from seeds during fermentation (Oszmianski and Sapis, 1989) and their source in grape skins, seeds and stems (Ricardo da Silva et al., 1992). While other studies have addressed their interaction with various proteins used for the fining of wines (Ricardo da Silva et al., 1991), the role that these components play in sensory and color stability is not fully understood.

There is some experimental evidence (Kantz and Singleton, 1990; Singleton and Trousdale, 1992) that the anthocyanins and procyanidin tannins are involved in the formation of complexes that help to keep both species in solution. This feature was thought to be important in retaining and stabilizing the pigments so that they are available to partake in the polymerization that occurs during aging, especially during the first year when most of the pigment polymerization takes place. It has now been established that the procyanidins are found in the grape skins of most red cultivars and are they are extracted during the fermentation. One important exception to this pattern is with grapes of Pinot noir which appears to lack the procyanidins in its skins (Thorngate, 1992).

The alternative view is that it is the monomeric phenols, rather than the procyanidins or larger tannins, which are responsible for the anthocyanin complexing, color enhancement and pigment stability, in what is referred to as copigmentation. There is little evidence that the polymers play a significant role in copigmentation and the results attributed to tannins using extracts may have been due to the accompanying phenolic monomers in these preparations. The role of dimers in the copigmentation phenomenon in wines has yet to be established.

The Role of Copigmentation

Our present understanding of the extraction of the anthocyanins compared to other flavonoids favours the interpretation in which the extracted anthocyanins quickly form stable couplings with a group of monomeric components, resulting in copigmentation complexes. The

effect of copigmentation is to allow additional anthocyanins to partition from the skins into the wine, resulting in higher total anthocyanin contents and more intense color. Many of the major monomeric phenols can act in this way, caffeic acid and its esters, catechin and epicatechin, and the flavones, myricetin, quercetin and kaempferol and many of these responses have previously been studied (Asen et al., 1972). All of these components, commonly referred to as cofactors, can cause copigmentation complexes to be formed and these have higher extinction values than the original anthocyanins. Some of them, the flavones for example, cause a shift in the maximum wavelength of 10 to 20 nm from red to blue. This phenomenon appears to be source of the purpleness in many highly-colored young red wines and between 30 to 40 % of the color of young red wines is due to copigmentation, Figure 6–1 (Neri and Boulton, 1996). Grapes which are low in these copigmentation cofactors, will not be able to form significant levels of copigmentation and will have correspondingly lower anthocyanin contents. This is true of cultivars such as Pinot noir, and Sangiovese, while others such as Merlot, Durif and Syrah have more copigmentation, contain more anthocyanins and are much deeper in color. One of the ironies in the color of red wines is that the levels of these non-colored monomers have a major contribution to their anthocyanin content and the color that they display.

Evidence that it is the monomeric components that are involved in copigmentation can be found in experiments in which colorless cofactors, added prior to fermentation have resulted in wines higher in anthocyanin content and higher levels of copigmentation and color. Further, using only analysis of the monomeric components, the color due to copigmentation has been predicted and is in good agreement with that measured in 25 wines from different cultivars. This would not be possible if self association of anthocyanins, complexes with procyanidins or complexes with larger tannins was the explanation for the color enhancement.

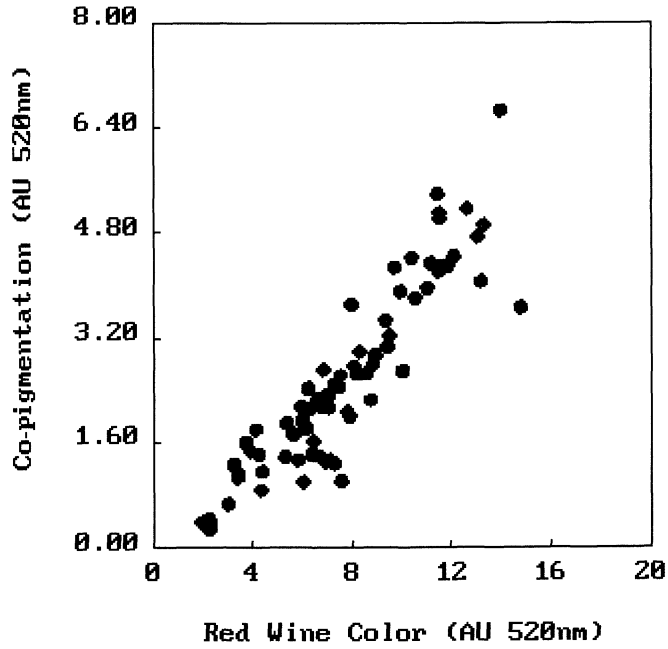


Figure 6–1 The fraction of red wine color due to copigmentation (Neri and Boulton, 1996).

The copigmentation is a dissociable equilibrium and this is progressively shifted as wines are diluted with a buffer. This is the cause of the no-Beer's law nature of young red wine color which was first noted by Boutaric et al. in 1937. They suggested that it was due to complexes between the pigments and other organic components in the wine and noted that there was variation between wines in the extent to which it occurred. It seems that all red grapes are limited in the levels of these cofactors and that the anthocyanins are generally in excess. The need and limitation of cofactors to form such complexes helps to explain why darkly colored grapes sometimes produce only lightly-colored wines, and why there is no relationship between the levels of anthocyanins in grapes and those in their corresponding wine.

The main copigmentation cofactors are flavonoid in nature and therefore found in the skins of red grapes. It is true that some of these components are also present in the skins of some white grapes, but they are not at significant levels in most white wines. This is because the juice is drawn off the skins prior to fermentation and some of the stronger cofactors have only low solubility. The possibility exists that the skins of certain white grapes could actually increase the color of a red wine if the red grapes have only low levels of these cofactors. This would be a special set of circumstances in which 1) the red grapes are low in cofactors, or had mostly weaker cofactors and the white is relatively high in them, 2) the skins are present during pigment extraction and 3) the white skins are in a minority in the mix. The need for the last condition arises from the adsorption of anthocyanins onto the white skins and the need to the color enhancement to outway the pigment depletion. The traditional practices in Chianti and parts of the Rhone Valley, where some white grapes are cofermented with red grapes, are good examples of this condition. The empirical mixture seems to be between 5 to 15 % white grapes and this depends whether whole grapes or only their skins are used. The results can be expected to vary from season to season.

The Rates of Component Extraction

The extraction of skin and seed components is thought by some to be a leaching process from a porous matrix rather than one in which equilibria are involved. There is a widespread belief that longer contact time provides further extraction particularly of color, when in fact this equilibrium has generally reached its final value by the third day of contact, provided good contacting between the juice and the skins has occurred. The slower release and migration of polymeric materials into wine cannot be entirely explained in terms of their slower diffusivity, and control of the rate resulting from changes in cell leakage and release reactions is indicated. It is instructive to reconsider the nature of these extractions in order that the effects of temperature and contacting technique on them can be understood.

The extraction curve for anthocyanins rises steeply initially, reaches a peak and then declines slightly during the remainder of the fermentation. Several studies (Ribereau-Gayon, 1974; Somers and Evans, 1979; Nagel and Wulf, 1979; Van Balen, 1984) show this general pattern. The extraction of other phenolic components (flavonoids, tannins and total phenols), however, shows an exponential approach to a final concentration (Van Balen, 1984). Figure 6–2 shows the extraction of flavonoids in a Cabernet Sauvignon wine at 22 °C with half of the final value being obtained by the end of the second day. If the extraction is simply the diffusion of pigments from the grape skin into the juice, the concentration would be expected to move exponentially towards the final level. The rate of extraction under this condition can be described by:

$$d[\text{Flavonoid}]/dt = k^*[F_e - F] \qquad (6.1)$$

which when integrated leads to the extraction curve:

$$[\text{Flavonoid}] = F_o + F_e^*[1 - \exp(-k^*t)] \qquad (6.1a)$$

where F_o is the initial concentration of flavonoids in the juice and F_e is the amount of extractable flavonoids in the skins. The rate constant, k, reflects the rate at which the flavonoids are extracted

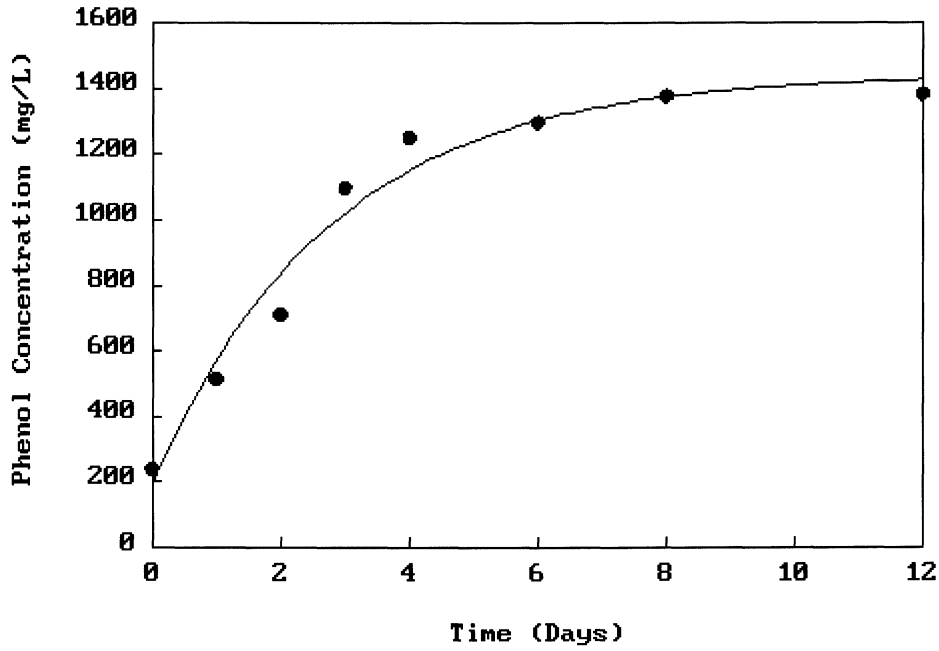


Figure 6–2 The extraction of flavonoids into a Cabernet Sauvignon wine (Van Balen, 1984).

and would be proportional to the diffusion coefficient of the molecules involved. Similar forms of this equation can be written for other extractable groups such as the polymeric phenols (tannins) and the total phenols. The initial concentrations, extractable amounts and the rate constants for the extraction during fermentation of a Cabernet Sauvignon (Van Balen, 1984) are summarized in Table 6–2. It can be seen that the rate of flavonoid extraction is approximately twice as fast as that of the polymeric phenols. The rate constant for the total phenols and the absorbance at 280 nm show slightly higher values because of the contribution of several components to these aggregate measures. The relative values of the rate constants are as might be expected from the molecular weight of the flavonoids and tannins. The faster constants might also be expected because of the contributions of smaller non-flavonoids to the total phenol and absorbance measures.

This exponential extraction pattern is not observed for the color pigments and other descriptions are required. One possible explanation for this is that there is a rapid extraction followed by a slower decline in concentration caused by the establishment of a secondary equilibrium involving the pigments, ethanol and other components. This is expected to be due to the establishment of copigmentation complexes and possible re-adsorption back onto skin and pulp tissue at moderate ethanol contents.

One of the few studies to analyze the extraction of the flavonoids in detail found little difference between the extraction rates of anthocyanins, their glucosides and their acylated forms, but these rates were significantly different from the extraction of catechin and epicatechin (Nagel and Wulf, 1979). The pigment extraction patterns reported by various investigators (Ribereau-Gayon, 1974; Somers and Evans, 1979; Nagel and Wulf, 1979; Van Balen, 1984) are well described by a two-term extraction model in which the initial faster exponential extraction is followed by a second but slower depletion to a

Table 6–2 The model constants for the extraction of flavonoids, polymeric phenols, total phenols, and absorbance at 280 nm into a Cabernet Sauvignon wine

Quantity	*Initial concentration F_o (mg/l, AU)*	*Extractable concentration F_e (mg/l, AU)*	*Rate constant k (h^{-1})*
Flavonoids	199	1253	0.0152
Polymeric phenols	19.2	643	0.0082
Total phenols	317	1210	0.0166
Absorbance at 280 nm	11.2	24.3	0.0193

Source: Van Balen (1984).

lower final value. In this situation the rate of extraction can be written:

$$d[A]/dt = k_1*[A_{1e} - A] - k_2*[A - A_{2e}] \quad (6.2)$$

where A is the anthocyanin concentration at time t, A_{1e} and A_{2e} are the equilibrium values for the first and second equilibria and k_1 and k_2 and are the apparent rate constants for the extraction and second irreversible equilibrium.

The concentration of anthocyanins in the juice at any time during fermentation is then described by the following relationship (assuming that no anthocyanins are present initially):

$$[\text{Anthocyanin}] = A_{1e}*[1 - \exp(-k_1*t)] - A_{2e}*[1 - \exp(-k_2*t)] \quad (6.2a)$$

The data of Ribereau-Gayon (1974) are shown in Figure 6–3 together with the best fit of the

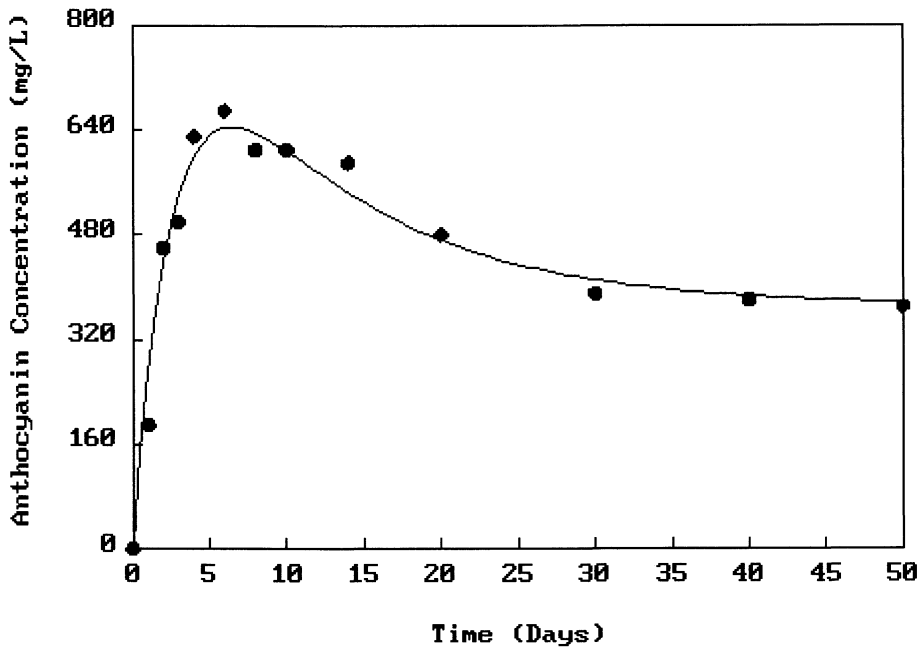


Figure 6–3 The changes in anthocyanin content during fermentation and extended maceration (Ribereau-Gayon, 1974).

proposed model for the extraction. The rate constants and anthocyanin values for this model are summarized in Table 6–3, together with the corresponding values for a number of other studies of this kind. The large variations in the magnitude of the rate constants suggest that they are not related to molecular diffusion and indicate that there are other factors that need to be accounted for in these extractions. One possible explanation would be the presence of reversible reactions within these equilibria and the involvement of components whose concentration is also changing throughout the extraction. The variation in the equilibrium levels also indicate that other factors are involved in the concentration of the anthocyanins that can be attained, presumably phenol fractions which are involved in the development of copigmentation.

This model of extraction describes the actual changes in the anthocyanin concentration and not those of observed color. The dynamics of the observed color are more complicated, being a result of at least three main effects. The first is the formation of copigmentation between anthocyanin and flavonoid cofactors. The second is the color loss during fermentation resulting from the solvent effect of the increasing ethanol concentration during the fermentation (Somers and Evans, 1979). This may be an effect of ethanol on the copigmentation equilibrium. The third is the bleaching effect caused by sulphur dioxide, either added or produced naturally by yeast during the fermentation.

The 'tannins' are generally defined as polymeric phenols capable of binding with proteins and include the procyanidins as well as the non-flavonoid polymers. The extraction of tannins during fermentation lags behind that of the anthocyanins, displaying a two-term extraction model with first- and zero-order terms, in con-

Table 6–3 Model constants for the extraction of anthocyanins into wines

Source	*Temperature (°C) cultivar, component*	*Rate constant* k_1 *(day*$^{-1}$*)*	*Rate constant* k_2 *(day*$^{-1}$*)*	*Concentration (mg/l)* A_{1e}	A_{2e}
Ribéreau-Gayon (1974)	Not stated Not stated Total anthocyanin	0.319	0.0981	1200	842
Somers and Evans (1979)	Not stated Shiraz (Syrah) Total anthocyanin	1.39	0.690	1500	802
Nagel and Wulf (1979)	20–22 Cabernet Sauvignon Malvidin-3-glucoside	1.42	0.196	189	69.7
Nagel and Wulf (1979)	20–22 Cabernet Sauvignon Total anthocyanin	1.62	0.175	572	327
Van Balen (1984)	20–23 Cabernet Sauvignon Total anthocyanin	0.405	0.114	882	482
Van Balen (1984)	20–23 Ruby Cabernet Total anthocyanin	0.592	0.163	1230	625
Van Balen (1984)	20–23 Carignan Total anthocyanin	0.507	0.074	195	176

trast to that seen with anthocyanins: a rise to a maximum followed by a depletion to a final level.

One description of the rate of tannin extraction suggests that there is a diffusion term that depends on the wine concentration and a leakage (or dissolution) term that is independent of the wine concentration. The rate equation for such a system takes the form:

$$d[\text{Tannin}]/dt = k_3*[T_e - T] + k_4 \qquad (6.3)$$

where k_3 and k_4 are the first- and zero-order rate constants and T_e is the equilibrium tannin concentration of the diffusional extraction.

The extraction during fermentation and during 50 days of extended maceration (Ribereau-Gayon, 1974) and that from seeds alone (Singleton and Draper, 1964) show a similar pattern and both are described by the integrated form of equation 6.3:

$$[\text{Tannin}] = T_e*[1 - \exp(-k_3*t)] + k_4*t \qquad (6.3a)$$

The rate constants (k_3) and (k_4) are 0.0130 and 0.0009 for the tannin extraction during fermentation (Figure 6–4); the values for the seed extraction alone are given in Table 6–4. It appears from the similarity of the extraction patterns that much of the tannin extraction that occurs during extended maceration may be coming from the seeds rather than the skins as has generally been believed.

Extraction From Seeds

The effect of temperature and ethanol on the extraction of tannin from seeds has been studied but given relatively little attention in many current discussions of tannin extraction in red wine making. The application of the kinetic description presented here to previous seed extraction results (Singleton and Draper, 1964) show that the measured extraction of tannin from seeds is well accounted for by the diffusion and dissolution model. The corresponding rate constants for the water and model wine solutions are presented in Table 6–4. The extraction of tannin into the model wine solution at 20 °C is shown in

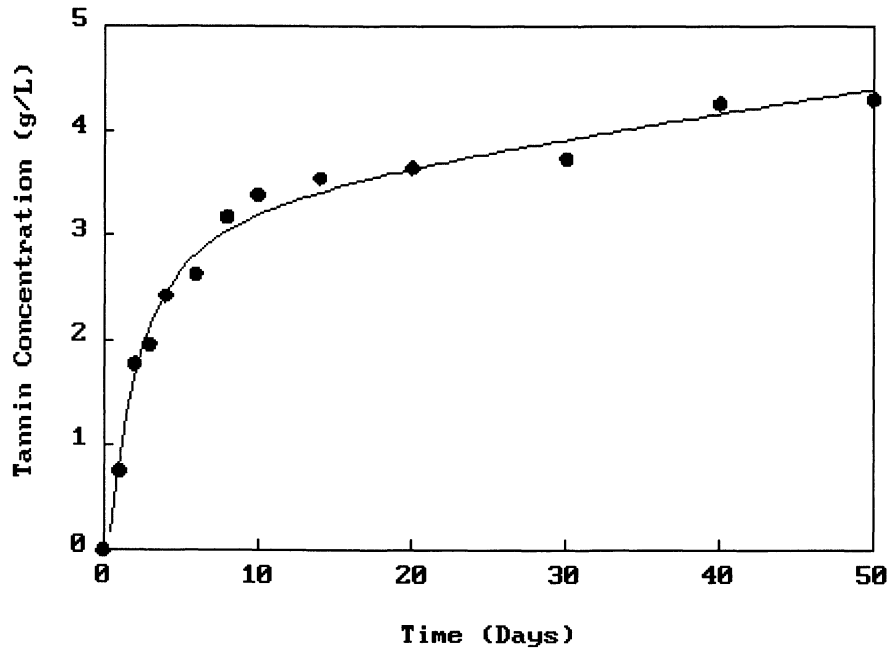


Figure 6–4 The extraction of tannin during fermentation and extended maceration (Ribereau-Gayon, 1974).

Table 6–4 Effect of temperature and ethanol content on the extraction of tannins from grape seeds

Temperature (°C)	*Rate constant* k^3 *(% h^{-1})*	*Rate constant* k^4 *(% h^{-1})*	*Equilibrium concentration* T_e
0% Ethanol			
11	0.0999	0.0943	25.03
20	0.0409	0.0550	42.40
30	0.0656	0.0614	48.17
14% Ethanol			
11	0.0382	0.0761	41.19
20	0.0319	0.0482	64.28
30	0.0375	0.0780	75.29

Source: to come.

Figure 6–5. The non-linear correlation coefficients are better than 0.99 in all cases. The main effect of temperature is seen in the equilibrium concentration, T_e, and except for the 11 °C water case, the diffusional constants are quite similar in value as might be expected. The dissolution constant, k_4, shows more variation, however, with no consistent temperature effect.

In practice, there will be considerable variation in the number of seeds per berry and the tannin levels per seed. The seed number is determined in the earliest stages of berry development, long before veraison and probably influenced by root and environmental conditions long before climatic variables are usually recorded. The level of tannin in the seeds declines throughout maturity

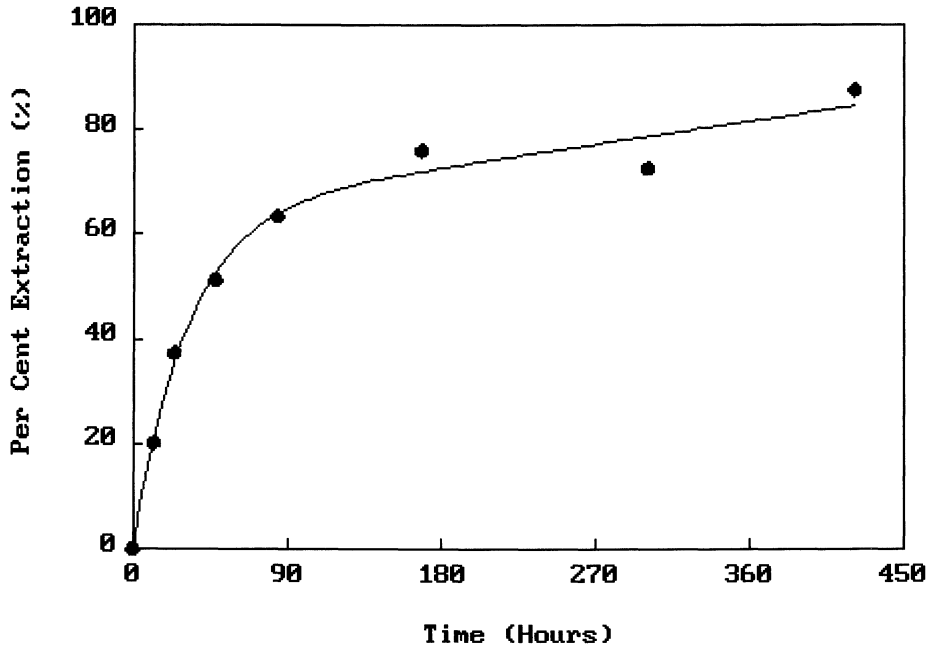


Figure 6–5 The extraction of tannin from grape seeds in a model wine at 20 °C (Singleton and Draper, 1964).

and seems to be changing little if at all by the time of harvest. The potential for tannin extraction is therefore quite variable due to site and season and the amounts actually extracted will be determined by the contacting conditions. It would appear that adaptive contacting practices are needed to allow for such differences, rather than the embracing of a certain method, as is often the case.

The Use of Temperature and Contacting Time to Enhance Extraction

The temperature of fermentation affects the extent of extraction in several ways. While effects on the rate constants are to be expected, there do not appear to be suitable extraction curves for the same grapes over a range of temperatures to quantify these effects. Although higher temperatures result in faster fermentations and ethanol formation, tannin extraction will also be faster. The impact of these extractions on the establishment of the anthocyanin equilibria is presently unknown. The data in Table 6–3 indicate that there are wide variations in the rate of anthocyanin extraction in different grape samples and it is difficult to draw conclusions regarding the relative contributions of contacting temperature or the contacting technique. The temperature effect becomes significantly different at higher temperatures (above 35 °C) when extraction is more extensive and quite different equilibria are observed.

The alternative options for juice and skin contacting range from changing the volumes employed and frequency of 'pump-overs' to the use of rotary fermentors that provide the mixing during their rotation. Other approaches include the early use of whole clusters followed by treading and later punching down of the skin cap. Some groups favor more extensive contacting during the early stages of the fermentation while others attempt a more continuous trickling approach rather than regular pump-over operations. It appears that the variation in phenolic composition and seed number between loads of grapes continue to outweigh the differences resulting from extraction temperature and contacting methods.

The Choice of Time to Press

Perhaps as significant as the temperature of extraction and the contacting method is the timing of the separation of the skins and seeds for the liquid. While the anthocyanin extraction will have reached its limit by the third day, the tannin extraction from skins and seeds can continue beyond the end of the fermentation (Ribereau-Gayon, 1974; Siegrist, 1985) or until separation takes place. The timing of the separation can be used to influence the relative proportions of color and tannin in the young wine; however, desirable analytical values for these components are not usually measured or known. Such measures would be complicated by the anthocyanin copigmentation couplings discussed previously.

The most obvious criteria for the separation are then color, tannin content, taste, sugar (or ethanol) content and contact time. The ideal situation would seem to be one in which maximal color and an acceptable tannin level are reached at the same time. There are still questions as to what constitutes the ideal level of tannin since the levels needed for good taste may not coincide with those needed for good polymerization and color stability. Further, the different kinetics of these extractions outlined above and the variations that exist between grape composition would suggest that such a coincidence is likely to occur only by chance. Following the extraction during a particular fermentation poses a dilemma in that, while there are good analytical measures for anthocyanin (and tannin), there is not a good relationship between tannin level (or total phenol content) and the astringency of the finished wine, as indicated by tasting. Tasting for astringency during the fermentation is not productive because of the effect of unfermented sugars. Since the relative proportions of color and tannin will be quite variable between and within loads of any cultivar, most winemakers continue to base the timing of the separation and pressing on the sugar content or juice density. This is primarily an indicator of time with a component that includes some measure of

ethanol content. As an indicator of extraction, it is only slightly better than contact time alone. The actual astringency of the young wine will be modified by blending or fining with one of the protein fining agents during the months following the fermentation. Winemakers typically choose densities in the range of 5 to 0 Brix to draw the liquid off and to press the skins with the conventional maceration. The timing of the draw, when pre-fermentation contact has been employed, can be earlier, but it is often the same. This is because of the additional extraction of tannin during fermentation which is associated with the formation of ethanol.

In the past, the use of screw presses led to considerable differences between the free-run and press fractions, especially in terms of tannin and mineral content. Today, the widespread application of membrane presses has essentially eliminated the extensive skin tearing and unacceptable composition associated with the continuous-screw and moving-head presses. As a result, the press fractions are generally added back to the wine as it completes the fermentation, unlike older practices of keeping them separate.

THE ETHANOL FERMENTATION

The decision to harvest may be based on color, flavor sugar concentrations or for reasons such as weather conditions. In some instances, the juice may need to be adjusted to correct an imbalance or it may be treated with hydrolyzing enzymes to enhance either juice recovery or extraction of skin components.

Must Preparation

The most common adjustments are those involving the titratable acidity and pH of the juice. Juices low in titratable acidity (less than 7 g/L as tartaric acid) or high in pH (greater than 3.5) can be adjusted with the addition of tartaric acid. The levels of addition will generally include an allowance for the precipitation of potassium bitartrate during fermentation. It is this precipitation that will cause the pH to fall rather than the addition itself.

In juices that are high in titratable acidity (greater than 10 g/L as tartaric acid), the acidity can be lowered prior to fermentation. Rarely does the pH of these juices need to be raised but it is accepted as a compromise for the acidity adjustment. This is done by the direct addition of potassium carbonate or the fractional treatment of part of the juice with calcium carbonate in what is referred to as the 'double salt treatment' (Wurdig, 1988). The lowering of the organic acid level by calcium carbonate treatment is especially important if there is a high concentration of malic acid resulting from cool growing conditions or early harvest. The double salt method is the only chemical method for lowering of malic acid concentration (in conjunction with tartaric acid), and the changes that will occur later with the malo-lactic fermentation will be less extensive.

The addition of nutrients to ensure good yeast growth and an acceptable fermentation is less commonly practiced with red musts than with clarified white juices. However a number of wineries practice the routine addition of ammonium salts (usually as diammonium phosphate to achieve a target of 125 to 150 mg/L as ammonia) and thiamin (at levels of 50 to 75 μg/L) in an attempt to minimize the formation of hydrogen sulphide and to provide normal fermentation rates and completion. The relationship of the assimilable nitrogen (alpha-amino nitrogen plus ammonium nitrogen) content to yeast growth rate and the development of cell mass is clear, but that for the formation of hydrogen sulphide in low-nitrogen musts is conflicting (Vos and Gray, 1979; Thomas et al., 1993b) and varies with yeast strain. The recommendations for assimilable nitrogen levels have been based on studies of white juices fermenting at 15 to 20 °C. They are generally applied to red fermentations without regard to the effects of temperature on growth rate, cell yield and assimilable nitrogen requirements. This is particularly troublesome in regard to the formation of hydrogen sulphide, which is usually more pronounced at red wine fermentation temperatures (25 to 30 °C).

The addition of hydrolytic enzymes, such as one of the commercial pectic enzyme preparations, is practiced by some wineries for the enhancement of juice release prior to pressing. This practice was developed in the past when many production facilities used continuous screw presses and the press juice fraction was usually of a less acceptable composition because of extensive skin tearing. The motivation to get more juice release prior to pressing has been reduced with the widespread introduction of large capacity membrane presses in which skin tearing is far less of an issue. The difference between the composition of the free-run and press fractions from these presses is small in most cases.

The addition of sulphur dioxide to musts is based on the desire to inhibit the activity of the grape enzyme phenol oxidase, to hinder the growth of natural yeast and to kill natural bacteria prior to fermentation. Levels of addition are typically in the range 25 to 75 mg/L with an average of 50 mg/L. At typical juice pH, this is adequate for these purposes, but it is not sufficient for mold-infected juices or musts that are beginning to ferment naturally. The effectiveness of the addition is limited to the first 10 to 12 hours, since the extraction of pigment from the skins will quickly bind the free sulphur dioxide. The oxidase activity determines the level of dissolved oxygen that is available for uptake and utilization by the added yeast. Musts in which the oxidase activity is not reduced or suppressed will develop an oxygen-deficient yeast population that will have poor viability in the later stages of fermentation. This could be a cause of incomplete fermentations in red wines, although it is more common in white wine fermentations where the completion of the fermentation relies on the viability of the non-growing cells. At juice pH, the role of free sulphur dioxide is to inhibit the enzyme rather than to consume the oxygen by chemical reaction. This is because the rate of oxygen uptake by the enzyme is typically thousands of times faster than that of the sulphite ion, which is almost non-existent at typical levels of sulphur dioxide addition.

The practice of adding ascorbic acid (or its optical isomer, erythorbic acid) as an anti-oxidant to consume oxygen is not widely used with red musts. The rate of oxygen consumption by ascorbate is comparable to that of the enzyme in some musts, and it lowers the short-term browning by competing for the dissolved oxygen. There is a need for at least one half of a saturation of oxygen at the point of inoculation to ensure good yeast viability in the stationary phase and this is more difficult to control when ascorbic acid has been added. Ascorbic acid, however, has no anti-microbial effect and sulphur dioxide, even at lower levels, will still be required for this purpose.

There is particular concern in certain regions about the destruction of wine pigments by the laccase enzyme that is usually found in grapes that have been infected by *Botrytis cinerea*. Laccase is not inhibited by normal additions of sulphur dioxide and is more active than phenol oxidase on several substrates found in grapes. It will also oxidize the anthocyanins and uses ascorbic acid as a substrate (Dubernet et al., 1977). The detection of laccase activity in grape musts has received considerable attention and while there is a spectrophotometric assay that uses syringaldazine (Dubourdieu et al., 1984) it is of limited use because of poor sensitivity at lower levels of infection. The reason for this appears to be the competition for binding from the other substrates in the juice and this is especially evident at low enzyme concentrations. There are also ELISA-based assays for *Botrytis* infection in grapes (Ricker et al., 1991; Fregoni et al., 1993) but the relationship between *Botrytis* infection and laccase activity is not expected to be linear or consistent. A more useful assay for winemakers is to measure the rate of oxygen uptake in a juice sample that has been treated with 75 mg/L sulphur dioxide. This level of sulphur dioxide will inhibit the background activity of phenol oxidase by approximately 90 % but will not greatly affect any laccase activity that is present. This test procedure is specific for the laccase activity (rather than the quantity of mold that it came from), in the presence of its corresponding

substrate mixture and is quite sensitive even at low levels of activity.

Yeast Inoculation

The most usual practice has now become the addition of a prepared yeast culture of *Saccharomyces* to achieve the ethanol fermentation rather than relying on the natural flora that are present on the grapes. The main advantages gained are the consistency of the fermentation pattern, the earlier onset of active fermentation and the minimization of undesirable byproduct formation. The widespread availability of dried yeast preparations that can be reactivated in water or juice has eliminated the need for slow and extensive propagation systems and the practice of cross-inoculation from existing fermentations to fresh musts. Yeast are added to produce initial cell counts of 2×10^6 to 4×10^6/mL rehydrated in 40 °C water or grape juice.

Dried yeast preparations have been in widespread use in California since the early 1970s and are now generally accepted in most wine-producing countries. There are currently approximately 15 commercial preparations available and these now include the most useful selections from various enology institutes throughout the world.

The contribution of the yeast strain to the character of the wine is generally of secondary importance and this is especially so in the making of red wines. While it has often been demonstrated in limited testing that differences exist between strains, these differences are usually not consistent when tested over a wide range of juice and must conditions. The choice is usually based on a yeast that can begin the fermentation quickly, provide a minimum of components such as acetic acid, ethyl acetate, bisulphite and hydrogen sulphide and can complete the fermentation efficiently. Some of the earliest selections continue to be the most useful strains today.

The use of natural flora to conduct the fermentation still has its advocates and is used in some locations. The must treatments differ in these cases in that sulphur dioxide is not added and there is no attempt to control oxidative enzyme activity and its corresponding oxygen depletion. The onset of fermentation is generally delayed by several days as the natural yeast population builds up to the levels corresponding to those of inoculations and those at which active fermentation begins. Several studies have shown that a succession of dominant yeast populations occur during such fermentations, based on nutrient availability in the juice, the relative growth rates of the yeasts and their sensitivity to ethanol. Seasonal variations in the microbial environment of the vine, the incidence of molds and mildew and the impact of vineyard spray programs are expected to cause wide variations in the levels and make-up of the natural flora. This results in further variations in wine composition that would not be found if yeast culture had been added but these are generally at the expense of varietal character.

Fermentation Temperature

The fermentation temperature influences the rate of yeast growth and thereby the time course of ethanol formation. There are increasing rates of extraction of all phenolic components at higher temperatures, but, as discussed previously, this does not usually increase the solubility of the anthocyanins that are extracted and often there is little enhancement in color. The higher rate of heat release can lead to increasing temperature when inadequate cooling is available and this in turn can lead to the enhanced formation of undesirable by-products if a nutrient limitation exists. Examples of such components are hydrogen sulphide and acetic acid. The cessation of yeast fermentation caused by temperatures rising above 35 °C is rare today. The influence of fermentation temperature on the retention of varietal character appears to be secondary to that caused by the stripping associated with the volumes of carbon dioxide evolved. The existence of any varietal aromas in wines is because these components have very low volatility and are not readily depleted by gas evolution. They do, however, have sensory thresholds that are at very low concentrations. The major effect

of fermentation temperature appears to be caused by variation in the extraction of phenolic components other than the anthocyanins.

Concurrent Malo-Lactic Fermentation

The trend since the early 1970s has been for winemakers also to inoculate the red musts with a prepared culture of malo-lactic bacteria rather than to inoculate the wine after the completion of the ethanol fermentation. The purpose is to have this fermentation completed more rapidly, consistently and with less undesirable by-product formation than occurs in the young wine. The wide variation in the initiation and completion of the fermentation in young red wines even when prepared cultures are used continues to be a scientific and winemaking concern, especially in regions where the ethanol contents are typically 12 and 13 % by volume. While the existence of nutrient deficiencies in musts (and the addition of supplements) is now generally accepted for the yeast fermentation, the corresponding acceptance of nutritional deficiencies as a cause of poor bacterial growth and byproduct formation in wines is a recent consideration.

Inoculation of the must with malo-lactic bacteria avoids the inhibition caused by ethanol and possibly other yeast by-products later in the fermentation (Dick et al., 1992). The complex nutrient requirements of these organisms (Du Plessis, 1963; Weiller and Radler, 1976) is well established, and the must provides a much more complete nutrient medium than does the finished wine. The addition of sulphur dioxide to a must would normally be lethal to such a bacterial inoculation. In the case of clean fruit, the addition may be reduced or avoided or delayed for a day or so until the pigments have bound any free sulphur dioxide. At this point the antimicrobial effects are almost entirely removed and the culture will be more successful.

The improvements in the commercial malo-lactic bacteria preparations over the past decade (King, 1986; Kreiger et al., 1993) have made the introduction of the simultaneous yeast and bacterial inoculations a practice that is already in widespread use in much of the modern wine world.

Prediction of Fermentation Behavior

The fermentation of grape must by yeast is a special case of the ethanol fermentation. Musts have almost equal proportions of glucose and fructose and a total hexose sugar level of the order of 200 to 240 g/L. As a result wine fermentations take much longer than beer fermentations. Cell growth ceases when 50 to 75 % of the sugar has been fermented and the remainder of the fermentation is conducted by maintenance activity of the stationary phase cells. The nutrition and medium conditions that influence the cell viability during this final period are especially important in these fermentations. It is the nutritional uptake, besides that of oxygen or sterols, during the early stages of growth that influence the behavior of the stationary phase cell, although there are few significant studies of this relationship.

At the sugar levels that occur in musts, there is complete saturation of the sugar transport systems of yeast and there is extensive competitive inhibition of hexose transport. Most strains of wine yeast are glucophilic, that is preferring to transport glucose in a glucose-fructose mixture. They differ considerably in the extent to which they display this preference. As the ethanol level increases there is increasing non-competitive inhibition of cell growth and secondary effects on cell viability. Wine yeast vary in their sensitivity to ethanol during growth and the maintenance phase. The yeast growth continues until the assimilable nitrogen is depleted, and the juice nitrogen level, therefore, determines the extent to which growth occurs and thus the relative contributions of growth and maintenance activities to the fermentation rate and progress. The first kinetic model to account for all of these factors and to be capable of describing non-isothermal wine fermentations was presented in the late 1970s (Boulton, 1980). Present forms of this model can estimate the progression of juice density in the more commonly used Brix and

Baumé scales as well as calculating the evolution of carbon dioxide and the ethanol evaporative losses during wine fermentations (Williams and Boulton, 1983). This fermentation model has recently been used in conjunction with on-line measurements of commercial fermentation to interpret fermentation behavior.

Fermentation Problems

The two major problems encountered in red wine fermentation are the formation of hydrogen sulphide and, separately, acetic acid. The first study to draw a connection between the free amino nitrogen content of the juice and hydrogen sulphide production during fermentation of white wines was that of Vos and Gray (1979). A number of studies have made recommendations of levels of assimilable nitrogen that should be present for fermentation completion and these range from 120 and 150 mg/l as nitrogen; these values are again based primarily on white juice experiments. The extraction of nitrogen components from skins during fermentation would generally compensate for lower juice levels, but, in the absence of other values, these targets are still of use with red musts. The data of Vos and Gray (1979) show large variations in the production of hydrogen sulphide even at nitrogen levels of 150 to 250 mg/L and other factors such as the proportions of certain amino acids, the ratio of ammonia to amino nitrogen, the level of pantothenic acid and the level of glutathione are thought to be more important than nitrogen levels alone.

Another source of hydrogen sulphide production is the residue from elemental sulphur used in the vineyard for mildew control. While several investigators have shown that hydrogen sulphide is produced when elemental sulphur is added to fermentations (Rankine, 1963; Acree et al., 1972; Schutz and Kunkee, 1977), the levels used were multiples of the residues normally found at harvest. Residue levels less than 2 μg/L are found when sulphur is appropriately applied (Thomas et al., 1993a) and levels above 2 μg/L, are needed to produce sensorially detectable concentrations of hydrogen sulphide (Thomas et al., 1993b). Throughout the 1980s, the use of several demethylation-inhibiting (DMI) fungicides led to the virtual elimination of elemental sulphur in Californian vineyards. The recent development of Bayleton-resistant strains of powdery mildew has brought about the widespread return to elemental sulphur applications and the subsequent hydrogen sulphide problems when high residues are found on clusters. Unlike the preparation of white juices, elemental sulphur residues on red grapes cannot be lowered by clarification since the presence of the skins is required during the fermentation. As a result the formation of hydrogen sulphide from this source is more of a problem in red wine fermentations.

The formation of methane and ethane thiols is associated with hydrogen sulfide formation and these are easily oxidized to disulfides during aerobic handling. Since they usually fall below threshold levels during this oxidation, some winemakers have adopted such handling practices as a means of removing them. Unfortunately they undergo a very slow cleavage by bisulphite during aging, reappearing as the thiols several months later. This can occur during bottle aging and it is probably the reason for the occasional practice of airing red wines after opening them. A more concerning finding has been the detection of the formation of methyl thio-acetate along with the thiols and hydrogen sulphide during fermentations (Rauhat and Kurbel, 1994). These compounds while less volatile than methane thiol, and apparently below threshold levels, may form methane thiol by hydrolysis, presumably in the months following the fermentation. As such they are a potential source of the delayed development of the sulphury and so-called "reduced" aromas during cellar and bottle aging.

Little progress in the understanding of and compositional basis for the formation of acetic acid by wine yeast has been made in the 1990s. The current thinking is that it is related to nutrient imbalance rather than deficiency and that it is not related to assimilable nitrogen content. The prob-

lem is usually exaggerated during the warmer (and faster) red wine fermentations. There is a significant seasonal variation in the extent to which it forms and only a minor part of this variation can be attributed to yeast strain effects. The contribution due to bacterial activity even in the absence of air, is difficult to assess.

Heat Evolution

The heat released by the fermentation is enough to raise the temperature to well above 30 °C unless it is removed by a cooling system and ambient losses. The rate of heat release is of particular importance for red wine fermentations since it will generally be two to three times that of white wine fermentations. Contemporary fermentor designs favor external jackets rather than internal coils or plates, because they are easier to clean and there is less risk of coolant leaks into the wine. The jacket approach requires less labor but it is limited by being increasingly insufficient in larger fermentors.

The rate of heat removal by cooling jackets is generally proportional to the wall area of the fermentor while the rate of generation is proportional to its volume. For cylindrical fermentors of a given geometry, the area per unit volume decreases with the reciprocal of the fermentor diameter, that is a fermentor of twice the diameter will have eight times the volume but only four times the surface area. This relationship implies that the use of jackets is restricted to relatively smaller volumes (less than 100,000 L for red wines) since colder coolant temperatures are needed to achieve the same transfer rate by compensating for the lower specific transfer area of the larger fermentors (Boulton, 1979). The use of colder coolant temperatures requires progressively more energy consumption because of poorer refrigeration performance and increased losses.

The preferred cooling method is to use external tube-in-shell exchangers and to schedule periodic cooling in conjunction with the pump-over operation. This permits one or more fermentor volumes to pass through the exchanger twice each day with the coldest juice being contacted with the skin cap.

Gas Evolution

The high sugar content of grape juices leads to a proportionately higher volume of carbon dioxide released during the wine fermentation. The theoretical yield is 60 L of carbon dioxide at 20 °C per litre of juice fermented (approximately 40 L/L of juice and skins). At peak fermentation rates of 50 to 75 g sugar/L/day (6 to 8 Brix/day), the rate of gas evolution will be approximately 10 to 15 L/L of must, that is 10 to 15 times the must volume each day. The importance of this value relates to the design of both the fermentors and the fermentation cellar, in particular to that of the air intake system for the cellar. The worker exposure limit for carbon dioxide should not exceed the time-weighted average of 5000 ppm during an 8 hour day. The outside air requirements to achieve this (assuming an atmospheric level of 600 ppm) will require approximately 200 volumes of outside air for each volume of carbon dioxide evolved or 12000 volumes of outside air for each volume of must fermented. A far more acceptable solution to this gas handling problem is the ducting of fermentor headspace gas directly out of the building rather than allowing it to overflow in the cellar. Such ducting should be stainless steel with sanitary connectors for ease of handling and cleaning. This approach has been implemented in only a few wineries but is relatively rare even in contemporary designs. Increased awareness of the working environment and the energy load involved in the introduction of such large volumes of outside air will hopefully resolve this situation.

The gas released during the fermentation is generally saturated with both water and ethanol vapors from the wine. Red wine fermentations give much higher ethanol losses because of the higher fermentation temperatures and these range from 550 to 1060 mg/L at 20 and 30 °C, respectively (Williams and Boulton, 1983). The emissions are even higher when the skin cap is warmer than the juice.

MALO-LACTIC FERMENTATION

The malo-lactic fermentation is the conversion of malic acid to lactic acid by certain lactic acid bacteria. The fermentation is a natural and traditional practice that generally occurred in the barrels during the spring following the harvest. It has traditionally been conducted by natural bacteria present in the staves of the barrels and there continues to be a carryover of this resident population from season to season in some older cellars.

The levels of malic acid in many red grapes range from 2 to 4 g/L. The concentration is influenced by berry size and malate respiration during ripening, and cooler growing conditions lead to higher concentrations. The fermentation usually results in a pH rise of between 0.1 and 0.5 units, proportional to the malate concentration and higher at higher pH levels. The carbon dioxide formed by the fermentation is 0.33 g per g of malic acid converted (or 0.18 L/g at 20 °C) and this release leads to the practice of loose-bung closing of the barrels until it is completed. The associated lowering of acidity is usually accepted in order to have the malic acid removed from the wine but there is a misplaced belief that by having this fermentation subsequent bacterial growth is prevented. In practice there is adequate nutrition for malo-lactic and spoilage bacteria to grow in many wines that have completed the fermentation. The relative importance of malate removal, nutrient depletion and bacteriocin formation in preventing subsequent bacterial spoilage is still not clear.

The acceptance of the fermentation is largely the result of the practical inability to prevent it in many wines, especially young red wines when the monomeric pigments are at their highest level. The anthocyanin pigments form colorless addition compounds with the bisulphite form of the free sulphur dioxide and at equilibrium almost all of the limiting component (pigment or bisulphite) is completely in the bound form. One estimate is that at a free sulphur dioxide level of 5 mg/L, 56 % of the anthocyanin monoglucoside would be bound. In a young red wine, the anthocyanin content is of the order of 300 to 500 mg/L and at wine pH almost all of the free sulphur dioxide is in the bisulphite form. The wide variation in actual pigment levels between wines leads to a wide range in the free levels at a specified addition. As a result, the more usual practice is to maintain only small levels of free sulphur dioxide during the first 6 to 8 months of aging until some 50 % or so of the pigments have polymerized, and these low free sulphur dioxide levels are usually not adequate to prevent the fermentation.

There are a number of studies that have shown an effect of the initial inoculum level on both the speed and the success of the fermentation in wines. Low levels of inoculation generally have poor viability while those ten times higher usually are successful. This suggests that there are components in finished wines (other than ethanol) that are inhibitory and their effects can be diminished by the larger inoculum levels but at additional expense. The observation of interactions between yeast and malo-lactic bacteria is not new (Fornachon, 1968; King and Beelman, 1986; Wibowo et al., 1988) but the agents responsible have not previously been recovered and shown to be responsible. The recent isolation of proteins produced by *Saccharomyces* which inhibit malolactic bacteria (Dick et al., 1992), is particularly important in this respect. The levels of these compounds in wines and the conditions under which they are produced need to be investigated further.

Malo-Lactic Bacteria

The preferred malo-lactic bacteria are generally strains of *Leuconostoc*, although strains of *Lactobacillus* and *Pediococcus* can also perform this conversion. The practice of inoculating wines with bacterial cultures to encourage this conversion was established in California many years ago (Webb and Ingraham, 1960). Since that time there have been many studies of the organisms involved, the enzymology of the conversion, the byproducts formed and the conditions that favor the successful growth of the culture. Two recent reviews of the microbiology of the lactic acid bacteria associated with the fer-

mentation are those by Wibowo et al. (1985) and Van Vuuren and Dicks (1993).

While most of the malo-lactic fermentations in red wines are completed without significant contributions to aroma and flavor, they continue to be a source of microbial spoilage in some wines. The inability to predict or control elevated levels of diacetyl, acetic acid and other unwanted components in certain wines remains a limitation in the routine acceptance of the fermentation as always beneficial. While there have been considerable advances in the microbiology of these organisms (Radler and Brohl, 1984; Wibowo et al., 1985; Van Vuuren and Dicks, 1993), there continues to be a need for more specific studies of the role of nutrition on their growth and metabolism in juices and wines.

Bacterial Nutrition

Perhaps the most poorly understood aspects of this fermentation remain the nutritional requirements of *Leuconostocs*, especially at pH values in the range 2.8 to 3.5, and the relationship between cell growth and the onset of the malic acid conversion. While a number of defined media (Du Plessis, 1963) and apple and tomato juice media exist, these are generally at pH values of 4.5 or above. More defined studies of this fermentation are required rather than the collection of wine-specific results from the literature.

Despite the general requirements for nicotinic and pantothenic acids of many malo-lactic bacteria (Weiller and Radler, 1972) and general decomposition of arginine, glutamic acid, histidine and tyrosine (Weiller and Radler, 1976), it is rare for nutrient additions to be made to wines to enhance the growth of prepared cultures. This may be because of the widespread belief that nutrient depletion is an important aspect of future stability and that making specific additions somewhat defeats this intent. The general practice has been to grow or adapt the culture by using a propagation medium and there continue to be variable results with commercial cultures (King, 1986; Kreiger et al., 1993).

Immobilized Bacteria

There have been significant advances in the preparation of immobilized columns of lactic acid bacteria (Spettoli et al., 1982; McCord and Ryu, 1985) that can convert malic to lactic acid. However, there does not appear to be any commercial application of these columns at present. Use of such columns would not have the nutrient depletion and possible bacteriocin production associated with the growth of cultures and, as a result, there are concerns about subsequent bacterial activity. The short-term life of such columns is a major limitation and controlling this is hampered by poor understanding of the cellular requirements for long-term survival in such a system.

POST-FERMENTATION HANDLING OF WINES

Red wines are usually transferred directly to barrels at the completion of the fermentation and the extent to which they are clarified at this point depends on the need to encourage the malo-lactic fermentation in the following weeks. Clarification may involve centrifugation or filtration to minimize the lees and sedimentation within the barrels or decanting the clarified fraction from a natural settling. The value in deliberately aerating the wine at this point continues to be debated and the wide variations in the practice would seem to suggest that it is not a major factor in color stability or sensory attributes of the aged wine.

Some winemakers prefer to wait until the aging is completed before making a blend or applying fining treatments. The rationale is to wait to see how the individual components for the final blend have aged before committing them to fining. The disadvantages of this approach are that it will often take an additional period of time for the many components of the blend to fully equilibrate and that after the first year many of the color compounds are in polymeric forms. The importance of these polymeric color forms is related to their depletion during

the fining with proteins, which is primarily aimed at modifying astringency and taste. The proteinaceous agents (albumen, casein, isinglass, gelatin) are added to lower the astringency by adsorption of polymeric phenols collectively called the tannins. While these polymers have been extracted during skin, seed and cooperage contact they are augmented by the polymerization reactions that involve the anthocyanin pigments. In young red wines all of the color is in the monomeric forms and during the first 6 to 8 months about half of the monomers will have been incorporated into colored polymers (Nagel and Wulf, 1979). The adsorptive action of the protein agents is to favor coupling with polymeric forms and this will usually result in a loss of color if left until after the aging stage. In most young red wines there is so much color that the loss may not be noticeable. The concern arises for wines that will be kept for a number of years since their color will decrease and become completely polymeric with time.

AGING

Aging Reactions

The most obvious aging reaction involves the polymerization of the anthocyanins during the first year after fermentation (Somers, 1971). One study of this change (Nagel and Wulf, 1979) found that the polymerization in their Cabernet Sauvignon and Merlot wines was approximately two thirds completed within 8 months. The rate of polymer formation does not follow the same kinetics as the decline in anthocyanin concentration and there are other components involved. The slow onset of polymer formation followed by faster rates at intermediate times and then a slowing of the rate towards the end, suggests the role of reaction intermediates that are neither anthocyanins nor polymers. The poor separation and quantification of the polymer fractions prevents a more detailed kinetic analysis of these reactions. Molecular weights of the tannin pigments are approximately 1000 in young wines, up to 2000 after 5 years of aging and as high as 4000 after 20 years (Ribereau-Gayon and Glories, 1971).

The role of aeration and acetaldehyde in the polymerization reactions continues to be poorly understood, with conflicting experimental results and interpretation. In one series of experiments (Pontallier and Ribereau-Gayon, 1983), the effects of repeated aeration (i.e. oxygen saturation) and initial level of sulphur dioxide were reported. From this work, some groups have concluded that monthly aerations are beneficial, and maintaining low sulphur dioxide during aging is desirable to enhance the polymerization reactions by encouraging the formation of acetaldehyde. The limitations of this study were the use of wines which were partially polymerized (30 % polymeric pigment) to begin with and the changes were noted over a 4-month period. While the accelerated polymerization of anthocyanins in the presence of acetaldehyde has been demonstrated (Timberlake and Bridle, 1976), it is primarily true for the diglucoside pigments of the non-*V. vinifera* cultivars. Recent experiments showing the formation of reaction products of the monoglucoside anthocyanins at very high levels of acetaldehyde (Bakker et al., 1993) tend to support the view that, under wine conditions, the role of this mechanism would be insignificant (Somers and Wescombe, 1987). This is not the case in fortified red wines (ports) where acetaldehyde levels are high from the added brandy (Reader—this book). These acetaldehyde-anthocyanin condensation products are of a bluish hue, but a new class of brick-red pigments of defined structure which are formed during red wine aging has recently been identified. These are typified by Vitisin A which results from reaction between malvidin-3-glucoside and pyruvate (Romero and Bakker 1999).

One of the few studies in which the effect of temperature on the rate of polymer formation was examined is that by Somers and Evans (1986). They found that storage at 30 °C dramatically slowed the rate of anthocyanin decline and polymer formation but seemed to have little effect on the color measure when compared to

that of wine at the same point but held at 25 °C. They were able to show more extensive polymerization under an oxygen headspace than under nitrogen, but there were only small increases in the color measures. This again points to the anaerobic polymerization reactions as the major ones with only secondary effects resulting from the oxygen-related mechanisms.

Cooperage Considerations

There are several contributions made by the aging container to the aging of red wines. They include the extraction of wood flavors and aromas, the extraction of phenolic components that influence astringency and the potential for moderate oxygen pick-up during filling and topping operations. The practice of loose-bunging and periodic topping of the barrel is favored by some, while the use of tight-bunging and rotating the barrels through 45 ° to keep the bung wet and swollen is preferred by others. There is not strong evidence to support either practice as the level of extraction is the more important factor. The loss of volatiles during this time is unlikely because of the development of a vacuum in tightly bunged barrels (Peterson, 1976) and the time scale of several years for this to occur, as it does in the aging of distilled spirits. The selection of oak casks for the aging of red wines will, therefore, be determined by the extent to which these aspects are to be accentuated. The rate of extraction of phenolics from different types and ages of oak barrel has been shown to be exponential (Rous and Alderson, 1983), with the limits falling most quickly after the first use. A more complete review of cooperage alternatives is given by Singleton (1974). The trend towards the use of younger cooperage has led to styles of certain wines in which the oak aroma has become the dominant factor, sometimes overwhelming varietal contributions even in young wines.

Microbial Control During Aging

Throughout the aging period, there is a continual need for microbial control and this is generally exercised by the use of free sulphur dioxide levels in the wine. The porous nature of wooden cooperage and the volatility of the molecular form lead to evaporative loss of this protection with time. Periodic additions are required and the frequency is determined by the tightness of the closure (loose-bunging versus tight-bunging) and the temperature and humidity of the surrounding atmosphere. The prevention of unwanted yeast and bacterial activity is carried out by maintaining appropriate levels of molecular sulphur dioxide in the wine. The molecular form is the undissociated form of the free sulphur dioxide pool; the level necessary to kill quickly several wine organisms has been determined (Beech et al., 1979). The actual free sulphur dioxide concentration to achieve this is a function of the wine pH. The most troublesome organisms in red wines are the spoilage yeast *Brettanomyces* and the various types of bacteria, *Pediococcus*, *Lactobacillus*, *Gluconobacter* and *Acetobacter*; these can be controlled by suitable levels of molecular sulphur dioxide.

Evaporative Losses

The evaporation of wine from the barrels during storage is a significant consideration and the control of the atmosphere in the aging cellars will affect this. The evaporation rate can be expected to be related to the partial pressures of water and ethanol at the wine temperature and their concentrations in the surrounding air. The major component of the evaporation is water and the relative proportions of water and ethanol will have slight effects on the ethanol concentrations in the aged wine. The control of humidity within cellars requires that there are also small variations in temperature. The maintenance of high humidity can lead to condensation as the temperature falls below the dew point condition. One series of measurements of the evaporative loss from wine barrels has shown that at 15 °C the annual losses will be 5 % and 2 % at a relative humidity of 55 % and 85 %, respectively (Blazer, 1991). An alternative approach to minimizing losses has been the introduction of stainless

steel barrels into which thin staves of oak are placed to provide extractive components. These alternatives do not provide the porosity that will allow the desirable loss of other volatiles such as aldehydes and sulphides, during the oak extraction process.

PREPARATION FOR BOTTLING

When the wine has aged to the desired extent, it may be blended and prepared for bottling. In the months that follow, this preparation will usually include some degree of stabilization and clarification to prevent a precipitation in the bottle during the first year or so. The eventual precipitation of polymeric pigments with some associated potassium bitartrate is to be expected in all red wines because of the continual polymerization of the phenolic components and the colloidal nature of the physical stability. However, significant sediment in a young wine is usually viewed as a winemaking defect or caused by poor shipping or storage conditions. Although many wines will become brilliantly clear during aging, the general situation for red wines is for them to be filtered prior to bottling to remove suspended matter and most if not all microorganisms.

The extent to which red wines are treated to prevent the precipitation of potassium bitartrate has undergone some reconsideration. The general practice of storing red wines at ambient temperatures and the improvements in insulated and temperature-controlled transport have led to a less extreme treatment of such wines. The adoption of seeded-agitated stability tests for wines (Boulton, 1983) has enabled the individual holding capacity and potassium bitartrate stability of wines at warmer temperatures to be determined. This approach differs significantly from the saturation temperature approach developed by others (Wurdig et al., 1982) and from modifications in which the criteria for stability is based on generalized levels of supersaturation for various wine types (Ratsimba and Gaillard, 1988). Many wineries have moved towards stability criteria which are based on temperatures of 5 or 10 °C and for correspondingly warmer treatment conditions. There are many, however, who continue to use treatments and other stability criteria that are based on temperatures close to freezing conditions.

The stabilization of red wines with respect to potassium bitartrate has secondary implications for the stability of copigmented color components. While the involvement of pigments in the holding capacity of wines has long been recognized (Pilone and Berg, 1956; Balakian and Berg, 1968), the nature of the interaction and the disturbance of such by exposure to very low temperatures and partial salt removal were not well understood. It now appears that the bitartrate ions are acting as counter anions to the flavylium cations of the copigmentation stacks and that lowering of their concentrations such as that caused by precipitation can lead to a loss of color as some copigmented forms are dissociated. In some cases this can result in a delayed pigment precipitation after extensive precipitation.

The final filtration of red wines commonly employs tight earth or pad filters and, in many cases, membrane filters. The use of membrane filters with pore sizes of 0.45 or 0.65 μm for the complete removal of bacteria and yeast, respectively, has been common since the mid 1970s, especially for wineries choosing to avoid the use of microbial agents such as fumarate, sorbate or dimethyl dicarbonate (DMDC). One alternative approach is to consider red wines to be less susceptible to bacterial spoilage since they have usually undergone the malo-lactic fermentation and the nutrient levels required for bacterial growth are depleted As a result, the complete removal of bacteria by membrane filtration is not adopted and the levels are merely lowered by tight pad filtration, even one capable of collecting most yeast.

The less-preferred alternative to membrane filtration is the introduction of either a yeast inhibitor such as sorbate or more recently a short-lived additive such as DMDC that can actually kill yeast present. The difficulty with these approaches, apart from the question of

chemical additives, is that the dosage required is a function of the number of cells present. The addition of sorbate is ineffective against most bacteria that are present and subsequent bacterial activity in the bottle can lead to the formation of the 'geranium' odor caused by the formation of 2-ethoxy-hexa-3,5 diene (Crowell and Guymon, 1975). The levels of DMDC currently used for the killing of yeast (50 to 100 mg/L), are also ineffective against many of the bacteria that are found in wines (Ough, 1983) and strategies involving free sulphur dioxide and membrane filtration are still required. The bacteria population can be controlled by increasing the levels of sulphur dioxide, but the ability to maintain the necessary levels of free sulphur dioxide in red wines is limited because of binding by anthocyanins. The general trend away from high levels of all additives, and in particular from non-traditional additives, reinforces the application of membrane filtration for the removal of microorganisms from wines.

One troublesome aspect of the membrane filtration of some red wines is the adsorptive interaction between certain polysaccharides in wines with the synthetic materials of the filter. While the levels of polysaccharides in wines have been known to be influenced by growing conditions and yeast fermentation (Ussegho-Tomasset, 1976) recent studies which have characterized polysaccharide fractions related to yeast (Llauberes et al., 1987) and bacterial activity (Llauberes, 1990) and those specific to red wines (Brillouet et al., 1990; Belleville et al., 1991) are particularly interesting. The identification of such fractions may lead to wine treatments based on enzymatic hydrolysis or selective adsorption and assist in the selection of alternative polymers for filter construction. The role that these polysaccharides play in the pigment stability of red wines has yet to be determined, even though studies have shown them to play a role in the inhibition of nucleation and crystal growth during tartrate crystallization, as might be expected.

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7

Sparkling Wines

Patricia Howe

INTRODUCTION

Dissolved carbon dioxide in wine, introduced by external addition or by internal fermentation, affects the human perceptions through all five senses. The "sparkle" in the wine can be perceived by the sight of bubbles rising through the liquid and a collar of foam ringing the glass, and by the faint crackling sound of the gas escaping. This escaping gas may entrain aroma molecules and increase their concentration in the headspace above the wine, increasing its effect on our sense of smell. The dissolved gas changes the taste perceptions of acidity, sweetness, and astringency; and finally, the prickly tactile sensation of the dissolved carbon dioxide is generally regarded as thirst quenching and may depend on pain pathways for its effect. This complex interrelationship of the carbon dioxide with our perception of the wine is a fascinating aspect of sparkling wine consumption, and usually is the primary motivation for the underlying winemaking decisions when choosing production methods.

Nearly every effort to describe sparkling wines begins with an attempt to categorize the many different methods used to produce them (Amerine *et al.*, 1980; Amerine & Joslyn, 1970; Armstrong *et al.*, 1994; Iland & Gago, 1997; and Robinson, 1994). To begin with, the wine to which the carbon dioxide is added, referred to as a "base wine," may be any fruit wine; this chapter will deal only with the wines made from the grape. These sparkling grape wines have many names, and their differences are dependent upon at least eight variables in the method of production. In addition to the production methods, several other factors determine the name used to describe the end product: the type of base wine used, local tradition, and complex legal regulations, to name a few. Most texts emphasize four main methods: carbonation, bulk fermentation (the Charmat method), bottle fermentation with filtration (the transfer method), and the classic champagne method. However, worldwide production techniques for sparkling wines differ in several details and demonstrate many more permutations than the common four methods. Nearly all of the wines made with residual carbon dioxide can be classified by eight production variables:

1. the type of grape base wine used,
2. the method of gaining the carbonation,

3. the sugar source for the carbonating fermentation,
4. the vessel used for the carbonating fermentation,
5. the amount of time of aging on fermentation yeast lees,
6. the method of clarifying the wine,
7. the final product container, and
8. the method for obtaining any remaining sugar in the finished product.

This is a much more complex classification system than normally applied. Although some of these methods are used rarely or only on small volumes, it is useful to be aware that they exist, and that they have been used commercially or historically. The classification system also calls attention to styles that perhaps have not yet been used on a commercial level, or if they have, for which a name has not yet been applied or has been forgotten. It also emphasizes the universal appeal of the effect of carbonation in a beverage; for one wine style to be made in so many different ways is a reflection of its desired qualities. The process names and styles resulting from the applications of different combinations of these variables are summarized in Figure 7–1.

BASE WINES

The production of the base wine used in making sparkling wines can follow any of the winemaking parameters discussed in other chapters. Any of the multitude of methods used in the determination of maturity, harvesting, crushing and pressing, pumping over, and addition of yeast, nutrients, fining agents, etc., are used for the production of the base wines; in addition, many different varieties of the grape, both red and white, aromatic or not, with or without extending contact with the skins, are used in the production of one type or another of sparkling wines. In considering a wine style that contains such divergent products as Australian sparkling Shiraz and Italian Moscato d'Asti, there is inadequate space to discuss the production methods of the base wines. Considering that there is probably a sparkling wine made from any type of still wine that can be produced, this chapter will instead emphasize the techniques that are unique to adding the sparkle to the wine.

Sparkling wines can be (and have been) made from base wines of virtually every type; they are fermented at least once and usually twice, and are bottled at least once and frequently twice. This augmentation and duplication of the winemaking process increases the requirement that the winemaker demonstrates the utmost skill.

Sparkling wines are frequently characterized as having both fruit character from the grape and yeast characters from the secondary fermentations (Markides, 1987). However, what little work has been done correlating the sensory characteristics of the base wines to the finished sparkling wines has found that the sensory properties of the base wine do not permit prediction of the sensory properties of the resulting sparkling wines (de la Presa-Owens *et al.*, 1998).

CARBONATION

Levels and Terms

In the United States, a wine is legally considered a sparkling wine if the carbon dioxide content is above 3.92 grams per liter. Wines with carbon dioxide levels below this point are legally considered still wines, even though they may have perceptible carbon dioxide levels and may still taste "fizzy." International recommendations from the OIV place a maximum carbon dioxide level for still wines at 2 grams per liter (Recht, 1992).

There are many ways to describe types and levels of carbonation in wine. Most countries have legal definitions, but these definitions may not be consistent (Rankine, 1990). American definitions for terms such as "carbonated sparkling wines" and "champagne type", and those trying to describe various "fizzy" wines

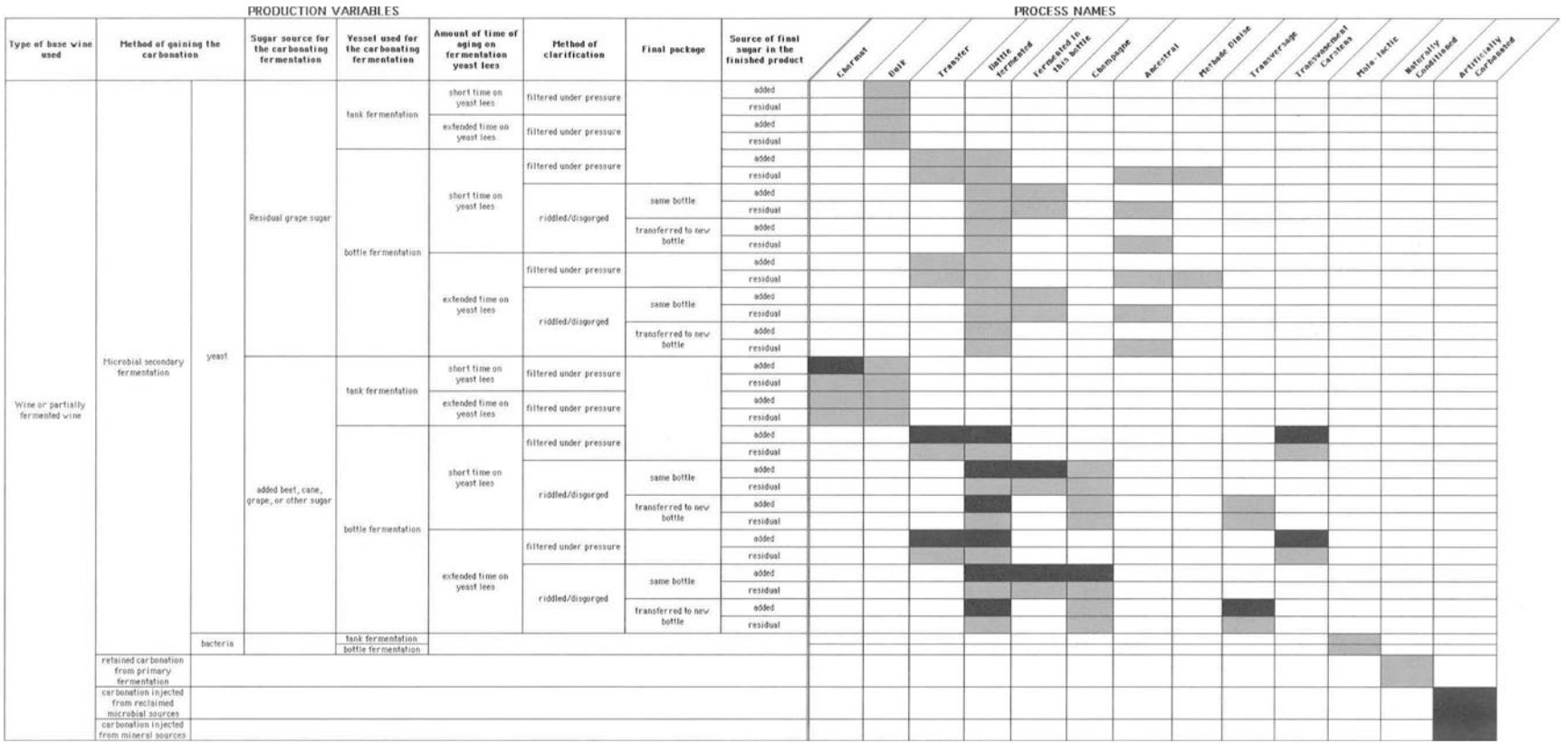


Figure 7–1 Eight key production variables in the manufacture of sparkling wines.

Notes: Black boxes show commonly accepted definitions. Gray boxes show possibly accepted definitions.

Charmat includes Charmat Process, Cuvé Close (Closed Tank), Tank Process, Tank Method, Fermented in Tank, Tank Fermented, "Méthode Charmataise," Autoclave, Granvas.

Bulk includes Bulk Process, Bulk Method, Fermented in Bulk, Bulk Fermented.

Champagne includes Champagne Method (Méthode Champenoise), Traditional Method (Méthode Traditionnelle) (Metodo tradizionale), Classic Method (Méthode Classique) (Metodo classico), Classic Traditional Method (Méthode Traditionnelle Classique), Fermentation en bouteille selon la méthode champenois.

Naturally Conditioned (not otherwise mentioned in the text) is used for some traditionally made ciders and beers.

such as "crackling wine," "cremant," "perlant," and "petillant" do not necessarily correspond to EEC-defined terms such as "Perlwine," "Cava," "crement," "mousseux," and "Champagne."

Quantification of Carbonation

The level of carbonation in a sparkling wine can be quantified in several ways. The measurement of the amount of internal pressure in the finished bottle at a given temperature, frequently expressed in units of atmospheres or bars, is perhaps the most common. Some methods convert pressure to volumes of carbon dioxide per volume of liquid product. Other methods have been developed that allow the expression of the carbonation in grams of carbon dioxide per liter of liquid. This requires measurement of the internal pressure of the finished bottle, the temperature, the alcohol of the final product, and the residual sugar, but allows direct comparison of carbonated products to levels of carbonation in "still wines," where carbonation is expressed in grams of carbon dioxide per liter of liquid. It is also a measurement that does not require expression of temperature (Jaulmes, 1973).

Methods of Carbonation

There are three primary methods for carbonating a sparkling wine. One is to retain the carbonation from the primary fermentation. Carbon dioxide is a natural byproduct of the fermentation of the grape sugars during the production of a base wine. If some of this carbon dioxide remains in solution in a wine at the time of bottling, the finished product may have a carbon dioxide level high enough to be considered "sparkling." This is usually an issue only in young white wines that have been tank fermented and bottled soon after fermentation has completed. If this carbonation is less than 3.92 grams per liter, it is considered still wine in the United States; European definitions would likely call this a "perlant" if the carbon dioxide ranges from 1 to 2 grams per liter. A perlant may also gain its carbonation from added carbon dioxide, rather than residual natural fermentation byproduct (Amerine & Roessler, 1983; Amerine *et al.*, 1980; Robinson, 1994).

A second carbonation method is to inject carbon dioxide either from reclaimed microbial sources or from mineral sources. Carbonation can be added to wine using a bulk carbon dioxide sparging system, similar to the production of other carbonated beverages such as soft drinks and some carbonated waters. Again, if a wine is carbonated to below 3.92 grams per liter of carbon dioxide, it is still considered a still wine in the United States. International definition of a wine with a minimum of 2 grams per liter carbon dioxide and a maximum of 2.5 bars of carbonation (from any source) qualifies it as "Perlwine" or "petillant" (Recht, 1992; Robinson, 1994). Carbonation is a relatively simple way to add carbon dioxide to a base wine. It generally requires that the base wine be clear and stable, and otherwise ready for a routine bottling. The temperature of the tank is normally dropped to facilitate the solubility of the carbon dioxide, and carbon dioxide is pumped into the wine until the desired concentration is reached. The wine is normally bottled cold using a counterpressure filler or other device that minimizes the loss of the gas during bottling (Amerine *et al.*, 1980; Armstrong *et al.*, 1994; Boulton *et al.*, 1996). The advantage of this direct carbonation is that it is quick, relatively inexpensive, and allows great control over the amount of carbonation to be added. The disadvantage is that the gas does not seem to integrate well into the wine, and it may form larger bubbles in the glass (Amerine & Roessler, 1983; Amerine & Joslyn, 1970).

The third method of gaining carbonation is through a microbial secondary fermentation. There are two types of agents for the secondary fermentation: bacteria and yeast. Bacterial fermentations usually involve conversion of malic acid to lactic acid and carbon dioxide, and do not produce high levels of carbonation. Lactic acid bacteria, such as *Leuconostoc*, *Pediococcus*, and *Lactobacillus*, produce carbon dioxide, which can be entrapped in the wine. If this

activity occurs during the production of the base wine and the carbon dioxide remains in solution at bottling, the finished wine may be considered "sparkling." The Portuguese Vinho Verde wines are an example of this style. The amount of carbon dioxide that can be contributed by this method is not high, and usually results in only a slight spritziness. This bacterial fermentation can occur either in a tank, with the carbonation being conserved at the time of bottling, or can occur in the bottle that goes directly to the consumer (Amerine *et al.*, 1980; Robinson, 1994).

SECONDARY FERMENTATION BY YEAST

The largest subset of sparkling wines is produced by the microbial secondary fermentation of yeast converting sugar to carbon dioxide and ethanol as in any other fermented beverage. This is by far the most complex and most traditional method of adding carbonation. Although any carbon dioxide that remains in a base wine after the completion of the initial fermentation of the grape sugars is usually allowed to escape to the atmosphere, fermentation activity of yeasts in a closed container traps the naturally generated gas in the wine and results in carbonation. This additional fermentation may be referred to as a secondary fermentation (not to be confused with the malo-lactic fermentation in the still wine production, which is also referred to as a secondary fermentation) or a "prise de mousse." The sugar source that allows the yeasts to produce the carbon dioxide may be either residual grape sugar from an incomplete primary fermentation, or added sugar from cane, beet, corn, or even grape sources. The yeasts themselves can be indigenous to the wine or added by the winemaker; they can be specially selected strains that agglomerate to each other to facilitate their precipitation; they can be contained within some type of membranous enclosure to prevent their escape into the wine.

Selection of Yeast and Conditioning

The fermentation of sparkling wines in a closed container is particularly difficult for yeast. Much discussion and research has gone into nutritional requirements for yeast in this situation. The yeast must certainly be tolerant to alcohol, and also tolerant to low temperatures, sulfur dioxide, and pressure. Because of the adverse conditions of temperature and ethanol, the oxygenation of the yeast culture, which has been determined to increase cell wall and membrane strength and increase the ethanol tolerance of the yeast is critical (Monk & Storer, 1986). Additions of lipid to the growing culture will also accomplish this ethanol tolerance; it also increases acetate and ethyl esters and fusel oils in the resulting wines (Rosi & Bertuccioli, 1992. Ethanol tolerance is considered the most important aspect in selection and conditioning of the strain for secondary fermentation. Traditional culturing methods for increasing the tolerance to alcohol include growing the culture at low temperatures (Valade *et al.*, 1985b). Proton flux measurements have been applied to glucose metabolizing yeast; those with sufficient ATPase activity to allow measurement can allow for a quick 30-minute determination of alcohol tolerance to within 0.6 % ethanol (Juroszek *et al.*, 1987b). These measurements support the traditional methods of conditioning yeast to low temperature as a method for increasing ethanol tolerance (Juroszek *et al.*, 1987a). As with base wine fermentations, aerobic growth of the culture encourages ethanol tolerance (Monk & Storer, 1986). Other nutritional elements, such as ammonia and other micronutrients, have been added to increase the ability of the yeasts to perform their task. Factors other than ethanol that limit ability to ferment include oxygen level, amino acid content, fatty acids levels, sulfur dioxide, pH, temperature, and level of inoculation (Valade *et al.*, 1985a; Monk & Storer, 1986).

Fermentation Temperature

The temperature of fermentation is particularly important in most traditional methods, as

lower temperatures increase the ability of the carbon dioxide to remain in solution, but also adds an additional strain to the yeast. The coefficient of absorption for carbon dioxide varies in inverse relation to the temperature, and the proportion of carbonic acid in solution is more considerable in secondary fermentations at cooler temperatures (Boulton *et al.*, 1996). If the temperature rises too high, poor carbon dioxide absorption and greater bottle breakage will be the result (Amerine *et al.*, 1980). The limits of livable temperature range are from 10 ° to 25 °C for most of the champagne yeasts. Increasing fermentation temperature from 10 ° to 20 °C increased final cell mass by double (Hardy, 1993a). A constant and habitable temperature is much more important for the carbonating fermentation than it is for the primary fermentation.

Culturing Techniques

Different types of culturing techniques are used. A wet culture, grown from a slant from a collection, is typical. Use of active dry yeasts has increased as selection and availability has expanded over the past 20 years. Dry yeasts must also be rehydrated and also conditioned appropriately using aerobic culturing techniques (Monk & Storer, 1986). No differences in wines have been found between those made from liquid and those from dried cultures (Valade *et al.*, 1985b).

Inoculum Size

Enough yeast culture is needed to complete the fermentation under adverse conditions, but too much yeast would result in the overly rapid fermentation and/or yield a wine with a disproportionate aroma of fresh yeast (Valade, 1985a; Monk & Storer, 1986). The standard level of yeast addition is one million cells per ml of wine and may vary with the expected fermentation temperature. Inoculum size will affect fermentation lag time, growth rate, and final cell mass (Monk & Storer, 1986). In bottle-fermented wines, an inoculum of 1.5 x 10^6 cells per ml yields an average of 8–10 x 10^6 cells per ml at a growth temperature of 10 °C (Hardy, 1993a).

Agglomerating Ability

A third factor in choosing the strain is agglomerating ability. Flocculent yeast forms a heavy sediment as opposed to the fine sediment of non-flocculating wine yeast. Recently, genetic techniques have been developed to select for this particular trait. A single dominant gene, *FL01*, can confer flocculation properties (Thorton, 1985). There are other practical matters to consider when using agglomerating yeast, such as how to count the cells and how to ensure that the culture is evenly mixed (Caillet, 1991).

Enclosed or Encapsulated Yeast

The enclosure of the yeast in membranous beads or immobilized gels to allow for complete control of the yeast has been developed and implemented in the past two decades (Yokotsuka *et al.*, 1997). A polymer of D-mannuronic and L-guluronic acid in a "double envelope" helps reduce possible leakage (Lallement, 1990). This technology can be used for bottle fermentations, tank fermentations, or even continuous applications (Krasny *et al.*, 1992). Immobilized yeast requires stabilization and filtration of the base wine (Lallement, 1990). No significant differences were found between encapsulated and traditional yeast. Leaking must be prevented by adequate inoculation (Yokotsuka *et al.*, 1997).

The Sugar Source for the Carbonating Fermentation

The sugar source for the carbonating fermentation can be from either residual grape sugar or added sugar, such as beet, cane, grape, or other sources. If the primary fermentation did not go to completion, and adequate sugar remains in the wine, this wine may be transferred to a closed container (such as the bottle) and allowed to complete its fermentation. This method is used under the names "*méthode rurale*" or "*méthode*

ancestrale" (Robinson, 1994). More commonly, the primary fermentation of the grape sugar is allowed to complete. Additional sugar is then added to the wine in a controlled manner from any of the common sugar sources. During the secondary fermentation of sparkling wine, yeasts convert sugar into carbon dioxide and ethanol. Pasteur demonstrated that 100 grams of cane sugar would yield 49.25 grams of carbon dioxide, or 24.9 volumes of carbon dioxide per volume of wine. Yeasts growing in anaerobic conditions require 4.0 grams of sucrose to yield one volume of carbon dioxide per liter (or 4.2 grams of glucose or fructose to yield the same carbon dioxide). If the desired product is a wine with six volumes of pressure, one starts with about 24 grams of sugar per liter of wine (Armstrong *et al.*, 1994).

The Vessel Used for the Carbonating Fermentation

The size and shape of the container in which the secondary fermentation occurs can affect the quality of the wine in several different ways. The relative amount of headspace to volume of wine can be a factor if the headspace contains oxygen. This can also be significant in bottle fermentations; unlike still wine bottling, it is unusual to sparge the empty sparkling wine bottles with inert gas prior to filling. Thus, the volume of the headspace in the bottle can relate directly to potential sources of oxygen during the fermentation. The same effect can be seen in tank fermentations.

This relative amount of headspace also can figure significantly at the time of disgorging, if that method of removing the yeast sediment is used. If the headspace volume in the bottle is inadequate to allow the internal carbon dioxide to pressurize this headspace with enough force to push the plug of yeast sediment out, the disgorging process will fail.

Another important consideration is the volume of the wine relative to the exposed surface area of the yeast. The geometry of the bottle or the tank may increase or decrease its exposed surface area. Mixing is sometimes used to increase the surface area and may assist in increasing the pickup of amino acids during the excretion phase. It is not believed to have any effect on autolysis (Colagrande & Silva, 1981).

YEAST LEES AGING

When the carbonation is generated by yeast fermentation in a closed vessel and the wine is left to age on the yeast lees, a complex series of reactions involving enzymes, proteins, amino acids, lipids, polysaccharides, and other macromolecules can significantly change the chemical composition of the wine and affect the aroma, flavor, and physical behavior (with respect to the foaming properties) of the wine. This aspect of sparkling wine production is considered as important to the sensory properties of the wine as the contribution of the grape flavors (Markides, 1987) and may explain why base wine sensory attributes are not predictors of finished wine attributes (de la Presa-Owens *et al.*, 1998). These reactions follow a generalized sequence, and the classification of the types of sparkling wines differentiate those wines that spend a short time on yeast lees and are primarily simply carbonated by the fermentation versus those wines that remain in contact with the lees long enough to gain significant sensory character from these reactions.

Overview of Lees Aging Reactions

The levels of amino acids in sparkling wines fluctuate slowly during the aging on the yeast, and it is these changes that are ultimately responsible for some of the effects on the aromas and flavors of the wine (Feuillat, 1981). During the secondary fermentation, the levels of amino acids initially decrease as the yeast rapidly absorbs them as a source of nitrogen necessary for growth. The yeast preferentially metabolizes certain amino acids because of their ability to convert them easily to other chemical structures. These preferences vary greatly between the yeast strains, and within one strain these preferences

may also vary with different growing conditions (Leroy *et al.*, 1990). As the yeasts run out of sugar and become stressed, they release much of the nitrogen back into the wine in forms different than those originally absorbed. This stage is usually reached within one or two months after the beginning of the secondary fermentation and is referred to as excretion (Suarez *et al.*, 1979; Ari'izumi *et al.*, 1994; Feuillat & Charpentier, 1982; Colagrande & Silva, 1981).

During the next four to six months, relatively little change occurs in the levels and types of amino acids in the wine. The yeast cells, although dead, remain whole and intact (Charpentier *et al.*, 1986). However, within the cells enzymes continue to react, slowly digesting the yeast cell walls. Most of these enzymes are intracellular proteases and slowly autolyze the yeast and therefore eventually cause the release of nitrogenous materials back into the wine. These materials are usually proteins, protein fragments such as peptides, and amino acids in various levels and forms. This level of amino acids then goes through a resting period of several months at normal fermentation temperatures of between 10 ° and 20 °C. This is followed by the reactivation stage, when enzymatic activity begins to be measurable again and amino acid levels begin to rise (Suarez *et al.*, 1979; Feuillat & Charpentier, 1982; Leroy *et al.*, 1990; Lurton *et al.*, 1989).

The enzymes continue to slowly react—even after eight years, the protease enzymes are capable of activity. From the time autolysis begins, these enzymes are constantly digesting the yeast cells and producing more amino acids from the breakdown of the yeast proteins. The actual volume of solid yeast material may decrease as much as 25 % of starting mass as the autolysis process digests the yeast (Colagrande & Silva, 1981; Charpentier, 1988; Leroy *et al.*, 1990).

The slow breakdown of the proteins of the yeast is demonstrated in the increasing level of peptides, a byproduct of the breakdown of proteins. The peptide concentration may be almost twice as high after four years on the yeast as opposed to one year. These protease byproducts then react with other wine components, such as tartaric acid, malic acid, alcohol, and other amino acids, and the levels of free amino acids fluctuate slowly over the next several years. Amino acids are continuously being released by the autolysis process, but these same amino acids become bound up and involved in other reactions. Amino acids are precursors to aroma or flavor compounds such as higher alcohols, lactones, polyamines, and amino acid esters, and the amino acids themselves may have a sweet taste. Large molecules such as proteins and peptides may bind with some normally volatile compounds and keep them in solution, thus reducing their possible contribution to the aroma of the wine. The amino acids cysteine and methionine contain sulfur, which can be freed if the amino acid is broken down. Many of the aromas of older champagnes are typical of sulfur-related aroma compounds, such as coffee and toasted nuts (Feulliat & Charpentier, 1982).

Lipid concentrations also continue to change during the aging on the lees (Lubbers *et al.*, 1994; Rosi & Bertuccioli, 1992; Troton *et al.*, 1989). Secondary and tertiary reactions of the amino acids and the lipids in the wine solution continue to develop aroma and mouthfeel characteristics. The carbon-dioxide emulsifying effects of these macromolecules also have a significant influence on the behavior of the foam and of the carbon dioxide.

Accelerated aging techniques have long been studied. The addition of heat while the wine is in contact with the yeast lees has never satisfactorily mimicked the effect of time. This seems to be related to the inactivation of some of the proteases at temperatures as low as 30 °C. It may be also that secondary reactions of the byproducts occur at different rates than the protease reactions. Other methods of accelerating the aging include yeast extract additions or mixing treatments. These processes do not speed up or increase autolysis, but may increase the amino acid content in the wine from enhanced excretion of existing amino acids from within the yeast cells (Colagrande & Silva, 1981; Feuillat

& Charpentier, 1982; Kelly-Treadwell, 1988; Molnar *et al.*, 1980).

Non-Enzymic Effects on Composition of the Wine with Lees Contact

The yeast walls present in the wine will also affect flavors. The vapor phase concentration of isoamyl alcohol, octanal, ethyl hexanoate, and ethyl octanoate all decrease when in contact with yeast cell walls. The binding is greater between the walls and hydrophobic molecules and appears to be related to the lipid content of the cell walls (Lubbers *et al.*, 1994). After six weeks of secondary fermentation, membranous compounds in the cell wall begin to degrade, and from three months onward all become plasmolyzed (Piton *et al.*, 1988). The polysaccharide content of wine also increases with six months' contact with primary fermentation lees. Mannan from the yeast combines with protein by co-precipitation; this varies with strain, temperature of storage, and time (Llauberes *et al.*, 1987). Lipid content of the wine also changes. Triacyl glycerides are released into the wine from the yeast and then undergo other reactions; oxidation of the triacyl glyceride fatty acids and rapid degradation into smaller molecules may occur, which could have flavor impacts (Troton *et al.*, 1989).

Esterification and volatile compound production after six months on yeast lees are affected by pH and titratable acidity. Ethyl hexanoate, ethyl lactate, diethylmalate, and octanoic acid increase with increasing titratable acidity; isoamyl acetate and phenethyl alcohol increase with decreasing titrable acidity. Increasing pH results in increasing isoamyl acetate, acetic acid, and octanoic acid but with decreases in ethyl lactate and diethyl malate (Paterson *et al.*, 1998).

Excretion of Amino Acids

Excretion is not to be confused with autolysis. Excretion is the initial flush of amino acids added to the wine during and just after the secondary fermentation and is a simple leaking phenomenon, not an enzymatic one. The first stage in the sequence of lees development requires the exhaustion of the sugar in the wine milieu (Charpentier *et al.*, 1986). At this early stage, the amino acid content of the wine increases as the yeast excretes the nutrients that had been initially absorbed during the fermentation (Feuillat & Charpentier, 1982). The amino acid concentration remains constant in the bottle from 3 to 12 months but begins to increase after that (Suarez *et al.*, 1979). The greatest amino acid concentration occurs at 6 to 12 months after fermentation. This increase in amino acids is a purely passive activity and does not involve enzymatic activity, and is thus not properly part of the autolysis process. The composition of the amino acids released will be different than those initially absorbed by the yeast.

Autolysis and Enzymatic Activity

Enzymatic activity decreases rapidly after fermentation, reaching a low point after about six months, and then increases (Feuillat & Charpentier, 1982). Intracellular protease and carboxypeptidases result in a slow increase in amino acids during storage on lees (Sato *et al.*, 1997). Hydrolysis of yeast proteins by proteases and peptidases begins several months after fermentation completes. The greatest concentration of amino acids occurs at 6 to 12 months. Decreases after this time are due either to further reactions that may lead to flavor precursors or to de-amination, especially of alanine and arginine (Feuillat & Charpentier, 1982). The pH of *méthode champenoise* wines is 2.9 to 3.2, which is conducive to the optimum pH of protease A, molecular weight of 7600; Protease A appears to be the most important at pH 3 (Lurton *et al.*, 1989). Although higher temperatures can increase the rate of protease activities, accelerated autolysis using heat may not yield comparable reactions (Kelly-Treadwell, 1988). Enzymatic processes are actually inhibited at the higher temperature of 45 °C (Feuillat & Charpentier, 1982), and low temperatures may promote favorable secondary chemical reactions (Kelly-Treadwell, 1988). Protease

activity in yeast during storage of sparkling wine decreased at 30 °C after about 40 days (Molnar *et al.*, 1980). Activity increased at 20 °C over that of 10 °C.

Extra cellular protease activities exist at or near detection limits and were therefore studied with lees concentrations of a hundredfold greater than normal concentrations (Sato *et al.*, 1997). Proteolytic activity stops after the second fermentation, then begins again after several months of storage, increasing steadily for two years with maximum activity at about six years (Leroy *et al.*, 1990). The protein content decreases and the amino acid content increases during the first month. The amino acids, especially aspartic acid, histidine, and lysine, increased in concentration until four months of aging (Ari'izumi *et al.*, 1994).

Autolytic ability is defined as the quantity of soluble nitrogen liberated by a known mass of yeast in a solution of hydroalcoholic medium of pH 3.5 at 37 °C for 48 hours (Leroy *et al.*, 1990). Autolysis is the loss of dry matter, with a decrease in the percentage of proteins and nucleic acids in this dry matter, and the presence of intracellular proteolytic activity (Leroy *et al.*, 1990). Loss of amino acids in the cell walls relates to the loss of glucosamine and phosphate; cell wall glucans also decrease due to the activity of glucanases; the cell walls remain the same thickness but become more porous and spongy (Charpentier *et al.*, 1986). Peptides and amino acids in bulk process wines increased relative to unheated controls when heated to 42 °C for either three or 72 hours; this phenomenon is excretion and is completely different from that produced by the ongoing contact with yeast cells (Colagrande & Silva, 1981). Soluble nitrogen, specifically amino acids, increases essentially during the secondary fermentation or immediately afterwards and is not a true indicator of autolytic activity (Leroy *et al.*, 1990). The reactivation phase corresponding to the reorganization of the cellular endostructure allows the release of lytic enzymes, particularly from the vacuoles (Leroy *et al.*, 1990). Thirty percent of the yeast nitrogen is released, about one-quarter of that as glutamic acid and alanine (Lurton *et al.*, 1989). Bulk fermented wines with added yeast and added disintegrated yeast increased in volatile compounds. Ethyl palmitate, ethyl palmitoleate, ethyl stearate, ethyl oleate, and ethyl linoleate concentrations all increased. Warming the temperature to "season" had little effect on the concentration of low-boiling-point compounds but did increase the high-boiling-point compounds; the effect was mixed on the concentration of terpenes. Warm temperatures had less effect on the disintegrated yeast additions (Molnar *et al.*, 1981).

METHOD OF CLARIFICATION

There are two options for clarifying the wine of the yeast cells and other detritus remaining in the tank or the bottle. Filtration under counterpressure and riddling (or *remuage*) are the two common methods. Riddling involves encouraging the sediment in a bottle into the neck of the bottle, which is then stored neck down; riddling is not an option for removing sediment from tanks.

No Clarification

Although this method (or lack of method) was used traditionally for bottle-fermented sparkling wines, it is no longer considered a commercial viability. However, prior to the introduction of filtration or riddling, all sparkling wines contained yeast sediment, and the drinking glass of this period was hollow stemmed, which allowed the settling of the sediment into the stem and allowed the clear beverage to be consumed from the top of the glass. The success in the beer industry of the yeast sediment–containing wheat beers and *hefeweisens* may indicate greater consumer acceptance than expected.

Riddling and Disgorging

Riddling, the labor-intensive and traditional method of removing the sediment from bottle-fermented sparkling wine, involves the turning and tilting of the bottle in a specially designed wooden rack (*pupitre*). The sediment (composed

of yeast cells and fining agents) and the air bubble (which is a result of the ullage in the bottle) are used to scrub the interior surface of the bottle, and the sediment is encouraged into the bottle neck (Hardy, 1993b). Mechanization of this process is common in all facilities, as the savings in time and labor have had no negative effects on the quality of the finished wine. The bottles are put into metal cages or wooden bins and placed in machines that turn the many bottles simultaneously in a process that mimics the hand-riddling motion (Hardy, 1993c). Once the sediment is in the neck of the bottle, the wine may be stored indefinitely.

The next step to removing the sediment is to freeze the neck of the bottle. An ice plug is formed in the neck of the bottle containing some wine and the yeast sediment. It is allowed to freeze solid. The bottle is then turned upright, and the plug of ice remains in the neck. Removal of the closure on the bottle allows the internal pressure to push the plug of ice out of the bottle, leaving the clear product behind.

Prior to the use of the freezing method, bottles were disgorged "on the fly" by carefully timing the removal of the cork or crown cap as the bottle was being turned upright. Just as the sediment begins to slide back down the neck, the bottle is opened, blowing the sediment out with a small amount of the wine.

Filtration

The ability to filter a sparkling wine to clarify it without losing the carbonation has greatly facilitated the production of large volumes of wine. The filtration can be done from tank to tank on tank-fermented wines, or can be done on bottle-fermented product that has been transferred under pressure back to tank. This bottle-fermented product may be filtered back to a bottling tank and then placed into new bottles.

THE FINAL PACKAGE

A small nuance in the classification system involves the final bottle. In tank-fermented products, it is clear that the final package was not the fermentation vessel. But bottle-fermented products can be categorized at least three ways. Bottle-fermented products that are clarified by filtration and returned to a separate bottle can be referred to as "fermented in *the* bottle"; this method is known as the transfer method. Bottle-fermented products that are clarified by riddling and disgorging but are then transferred to bottles other than the ones fermented in may also be referred to as "fermented in *the* bottle"; this method is also known as "*transversage*." The third method is a bottle-fermented product that is riddled, disgorged, and sold in the same bottle in which it fermented. This may be referred to as "fermented in *this* bottle."

SWEETENING

Some sparkling wines are naturally sweet at the end of the secondary fermentation, because of either a partial or an interrupted fermentation. These styles of sparkling wine rely on either residual natural grape sugar or residual added sugar from the secondary fermentation as a sweetener. This is probably the oldest method of sweetening. However, most sparkling wines are dry after the secondary fermentation. In general, these wines have low pH values, high acid levels, have relatively low alcohol concentrations, and benefit from an addition of sweetener. They are adjusted with the sugar addition at the time of bottling with a liquid sweetening solution called syrup or *dosage*.

The purpose of the syrup addition is to finish, address, smooth, and protect the sparkling wine. The interaction of the sweetness and the carrying liquid (the liquid in which the sugar was dissolved) with the sparkling wine can be complex. Sugar can affect the chemical solubility of aroma compounds. Sweetness levels can affect the perception of acidity, bitterness, and viscosity. The addition of brandy or of acid will also affect both the chemistry of the wine and the way humans perceive it. Syrups most commonly are a mixture of about 65 % pure sugar in grape wine, and usually contain sulfur dioxide or other

preservatives. Also allowed in the United States are grape brandy, grape concentrate, citric acid, ascorbic acid, tartaric acid, fumaric acid, and malic acid. A mixture of pure sugar and water other than wine is allowed, but it must have a sugar concentration of at least 60 °Brix. There are no US regulations dictating the sugar levels for each style of sparkling wine. The Committee Interprofessional du Vin de Champagne standard for sugar levels is a common reference, and many US wineries use it as a guideline. It is not just the absolute measure of the sweetness but the perception of the sweetness level that dictates the style. Two wines could conceivably have the same amount of sugar with one tasting dry and the other tasting semidry. The interaction of all the other wine components with the sugar prevents the use of the absolute scale and is reflected by the overlap in sugar levels between the styles (see Table 7–1).

AGING OF SPARKLING WINES IN THE ABSENCE OF YEAST—EFFECT OF HEAT AND LIGHT

General Sensory Effects of Heat

Moderate heat increases the evolution of the wine. It can be a benefit for a young wine to stay a short time between 20 ° and 30 °C, but longer times can have a negative effect. Heating Chardonnay and Semillon wine at 45 °C for three weeks yielded more oak, honey, and smoky characters at the expense of fruit aromas. High heat/short time (90 °C for up to 10 minutes) had no sensory effect (Francis *et al.*, 1994). Terpene glycosides are hydrolyzed by heat and can increase varietal aromas, but after an initial increase in floral aroma intensity, the floral monoterpenes are converted by hydrolysis and oxidation to odorless products or ones with high aroma thresholds (de la Presa Owens & Noble, 1997).

Heat and the Formation of Ethyl Carbamate

Due to the high concentrations of amino acids in some sparkling wines, the potential for the heat-induced formation of ethyl carbamate is very high (Stevens & Ough, 1993).

Heat and Maillard Reaction Products

Because of the addition of sugar syrup at disgorging, finished sparkling wines contain glucose and fructose. Heat-related reactions involving the sugars have been studied in connection with the baking of sherries. One heat byproduct of fructose is hydroxy methyl furfural, which has a chamomile-like odor and a slightly bitter taste. The high concentration of amino acids and the presence of the sugars and aldehydes make sparkling wine possibly susceptible to Maillard reactions; the relatively long storage times and the presence of alcohol, which lowers the water

Table 7–1 Relationship between Style, Sugar Levels, and Relative Taste in Sparkling Wines

Style terms	*CIVC dose (grams sugar/Liter wine)*	*Relative taste*
Natur, pas dose, Natural, undosed	0 g/L	Bone dry
Brut, Extra Trocken	0 to 15 g/L	Dry
Extra sec, Trocken, Extra dry	12 to 20 g/L	Slightly sweet
Sec, Halbsuss, polosladke, Dry	17 to 35 g/L	Moderately sweet
Demi-sec, Suss, sladke, Semi-Dry	33 to 50 g/L	Sweet
Doux, Sweet	More than 50 g/L	Very sweet

activity, may facilitate these reactions (Fennama, 1985). There is little published material on this subject.

Heat and Changes in Ester Composition

Ester stability is a dynamic process subject to the Law of Mass Action. At the end of fermentation, fruity esters produced from acetyl-CoA esterification of alcohols are generally in excess of their chemical equilibrium constants. Hence, many acetate esters hydrolyze back to the parent alcohols and acetic acid on aging, with a loss of fruity character. However, new esters such as ethyl lactate, which were originally below their equilibrium constants, can also form during aging. Both processes are favored by elevated temperatures (Ramey & Ough, 1980).

Heat and Oxidation

Sulfur dioxide is added to wines to prevent oxidation of phenols and aroma compounds. If there is no sulfur dioxide available to donate the electrons and be converted to sulfate, then ethanol may be oxidized to acetaldehyde (Marks & Morris, 1993). In wines treated with various combinations of SO_2 and ascorbic acid at the time of disgorging, and evaluated after 11 months, acetaldehyde was highest and browning was lowest when SO_2 was used. Ascorbic acid levels were 52–70 % of the original added amount, whether or not it was used in combination with SO_2 (Marks & Morris, 1993). Work at Domaine Chandon in California has shown that a 750-ml cork-finished bottle of bottle-fermented sparkling wine after disgorging and dosage addition and storage for one year at normal warehouse temperatures (about 14 °C) averages a loss of about 20 ppm total sulfur dioxide. About 5 ppm total sulfur dioxide is lost during the first 21 days at this temperature, or about 0.23 ppm per day, which correlates well with published findings (Ough, 1985).

Heat, Internal Pressure, and Bottle Seal

At a given temperature, 750 ml of the 12 % alcohol solution will increase in volume 2.3 ml per each increase of 10 °C (Boulton *et al.*, 1996). Depending on the orientation of the bottle, either the pressure in the bottle increases (cork down) or the headspace is slowly forced through or around the cork (cork up). When the temperature returns to normal, the pressure is relieved (cork down) or an equivalent volume of air is returned through or around the cork (cork up). Since about 20 % of air is oxygen, the latter position would in theory introduce oxygen to the wine. Repeat heating and cooling would be more detrimental to the quality of the wine because of the repeated introduction of oxygen. This raises some question as to whether the situation applies to sparkling wine, which is already under pressure; one would expect sparkling wine stored cork up to become flat if temperatures fluctuate. The increasing pressure with rising temperature may have other effects in sparkling wine that are less well understood, affecting the development of foam from the changes in dissolved carbon dioxide.

Heat and Protein Instabilities

Sparkling wines contain relatively high levels of proteins. Any or all of these proteins are denatured by heat; in fact, the test for protein stability is to heat the wine at a given temperature for a given time. Many sparkling wines are not stabilized against protein heat instabilities because of the importance of these proteins for breakdown into flavor precursors during aging (Brissonnet & Maujéan, 1993).

Light

Increase in the incidence of "light struck" aroma since the early 1970s may relate to the decrease in the quality of glass bottles, the increase in the use of flint (clear) bottles, or greater exposure of bottles of wine to fluorescent light (Dozon & Noble, 1989). Sulfur-containing

amino acids and riboflavin are photosensitive compounds; when exposed to light with wavelengths of 370 and 440 nm, a transfer of two protons from methionine to riboflavin occurs, resulting in the eventual formation of methanethiol and hydrogen sulfide (Maujean *et al.*, 1978). Changes in the sensory character of the wines can occur in as little as three hours at 35 mm distance from two 40-watt bulbs. Sensory changes are characterized by a decrease in citrus aroma and an increase in cooked cabbage, corn, wet dog, and soy/marmite aromas (Dozon & Noble, 1989).

FOAM AND BUBBLES

As would be expected in a product that is based on carbon dioxide, the measurement and quantification of foam and bubbles is an important aspect in sparkling wine.

Bubbles

The appearance of bubbles in a glass is an indication to the consumer that the wine is carbonated. The size and behavior of the bubbles are commonly accepted as indicators of the quality of the wine, smaller and more persistent streams of bubbles implying a higher quality. Although there are many factors in the production of the wine that will affect the behavior of the carbon dioxide, the quality of the tasting glass is probably more important to the appearance and the behavior of the bubbles than most production methods. Surface tension, carbon dioxide solubility, viscosity, density and depth of liquid, the partial pressure of carbon dioxide, and surface properties and dimensions of the container are factors that are most likely to determine the appearance of effervescence in sparkling wine (Casey, 1988). Experimental methods using strobe lighting have been used to study the cycle of bubble production in a glass (Liger-Belair *et al.*, 1999).

Foam

The ability of sparkling wines to form a foam (or "mousse") in addition to a simple stream of bubbles makes them special. Quantification and description of this foam were first required before an understanding of the underlying chemical cause and effects in the wines could be understood. The recent development of instruments such as the "Mosulux" and other techniques have facilitated quantification in the measurement of foam. This quantification allows for the investigation of the effects of macromolecules, lipids, and proteins on foam and mousse development. Compounds that increase foamability (the initial foam production) also decrease foam stability (the ability of the foam to maintain its form). Three types of measurements were determined to be important for sparkling wine: foam expansion, foam stability, and bubble average lifetime (Robillard *et al.*, 1993). Measurements of bubbles and foam correlated smaller bubble size with less carbon dioxide loss. Sugar, pressure, and wine color were also significant with respect to carbonation loss (Bach *et al.*, 1992). Some properties diminish with decreasing colloid or particle content; if particles are hydrophilic, steric hindrance and electrostatic repulsion could be the mechanisms involved. Wine proteins, which are positively charged at wine pH, could affect foam characteristics through these two mechanisms (Robillard *et al.*, 1993).

Understanding the impact of the base wine composition on the final foam performance has led to the evaluation of mono varietal base wines. Wines made from collected collapsed foam had higher foamability and foam stability, as did wines made from juices that had a high maturation index. Blending of mono varietal base wines can be used to control the foaming capacity of the resulting sparkling wines ("Cavas") (Lopez-Barajas *et al.*, 1998). In the base wines (those not yet subjected to the carbonating fermentation), foam stability relates positively to the content of the total linoleic acid (the sum of the free, unbound acid and that contained in all other forms). The foam height

correlates positively to the levels of tartaric acid and glucose; foam height correlates negatively to the level of proteins. In the Cavas (wines subjected to the carbonating fermentation), foam height correlates positively to the concentration of palmitic acid. Foam stability in Cavas relates positively to concentrations of protein, xylose, and polysaccharides, but negatively to total sulfur dioxide. The concentration of fatty acids has positive effects on the foam height and stability in the Cavas, while the concentration of proteins has mixed effects. This contrasts to findings in beer; the higher alcoholic content of wine or the distribution of the fatty acids as components of phospholipids, triglycerides, or lipoproteins may explain this difference (Pueyo *et al.*, 1995).

Champagnes (sparkling wines carbonated from a secondary fermentation in a bottle) produced by encapsulated yeast showed a large negative impact of base wine filtration on foam behavior. The filtration of base wine prior to the carbonating fermentation through a 0.2 μm membrane decreased foam in the finished sparkling wine; filtration through membranes of 0.45 μm to 3 μm, or unfiltered, had a less clear relationship (Viaux *et al.*, 1994). Hydrophobic proteins contribute more to foam composition than hydrophilic ones. In champagnes, the foaming proteins mostly range from 20,000 to 30,000 daltons in size; the proteins that contribute to the foam composition are small and acidic (Brissonnet & Maujean, 1991). Separating out the "foam wine" and the "remainder wine" and comparing them to the original base wine demonstrated that there is no effect of organic acids, titratable acidity, total nitrogen, calcium, potassium, magnesium, or sodium on the behavior of foam. Proteins, polysaccharides, and iron appeared to be important contributors to foam. Proteins may work according to the Bibb double-layer model to stabilize foam (Brissonet & Maujean, 1993).

CONCLUSION

The creation of wines containing carbonation requires effort and ingenuity. Traditional methods, which have proven successful over time for a particular grape wine type from a particular region, are vigorously protected by both legislation and convention. However, there is plenty of opportunity for developing innovative sparkling wine types and styles. New grape varieties, or those not traditionally used in sparkling wines, could create a whole new product, regardless of the method used to carbonate it. The traditional champagne method, perhaps one of the most protected, has continued to evolve since the beginning. The introduction of the process of blending wines, sugar additions, riddling and disgorging bottles to remove sediment, crown caps, automatic riddling machines, and recent work on encapsulated yeast demonstrates that even the most protected method continues to develop.

It is critical for those producing sparkling wines to understand why methods are developed and why they work, and to choose the best process for their particular wine. It is also critical to understand the relationship of product to process; neither exists in a vacuum (quite the contrary), and changing one variable may necessitate changing many others. But as long as the final sparkling wine continues to delight all the senses, we will know that we have succeeded.

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8

Fortified Wines Sherry, Port and Madeira

H.P. Reader and M. Dominguez

INTRODUCTION

Definition and Scope

Fortified wines, also known as liqueur or dessert wines, are produced by the fortification of fermented, partially fermented or unfermented grape must with wine-derived spirit. European Union regulations define liqueur wines generally as those having an acquired alcohol content by volume of between 15 % and 22 %, and a total alcohol content (*i.e.* acquired alcohol plus potential alcohol) of at least 17.5 % vol.; within these rules allowance is made for *vino generoso*, wines with 15.0 % vol. alcohol and less than 5 g l^{-1} sugar produced in demarcated areas (Council Regulation (EC) No. 822/87, 1987). This definition conveniently covers the types of wines discussed here, where we shall consider only those wines whose alcohol has been partially or wholly acquired by fortification. We shall use the terms fortified, dessert and liqueur, when applied to wine, indiscriminately. Flavored wine-based beverages such as vermouths will not be covered here, nor will we consider the production of fortified wines based on the processing and fermentation of grape juice concentrate.

We shall attempt here to give a view of present day technology of production of fortified wines, concentrating on Sherry, Port and Madeira as produced in their demarcated areas in Spain, Portugal and the Portuguese archipelago of Madeira, and describing historical and traditional practices only where these are still in significant usage or where they serve to illustrate the evolution of modern techniques. Many excellent works exist which cover the history and development (*e.g.* González Gordon, 1935, 1990, Fifield, 1978; Bradford, 1978; Cossart, 1984; Fonseca *et. al.*, 1987; Jeffs, 1992) and traditional techniques (Goswell and Kunkee, 1977) of the classic fortified wines, and the reader is referred to these.

We shall refer to wines produced in countries such as Australia, the United States of America and South Africa and based on the styles of the European wines, as 'Sherry-style', 'Port-style' etc. for reasons of clarity. Although, strictly speaking, Sherry, Port and Madeira are qualified to be titled as such only after receiving their appropriate Certificate of Origin, the terms will be used throughout their respective production processes. Techniques in the production of the several other traditional and excellent European

fortified wines, such as Sicilian Masarla, *Moscatel de Setúbal* (Portugal) and *Pineau de Charentes* (France), probably deserve a separate account, and we will mention them here only when they serve to illustrate better our discussion of Port, Sherry and Madeira.

Production of Port, Sherry and Madeira is subject to complex regulation; beyond the European Union Regulations for liqueur wines (Council Regulation (EC) N° 4252/88, 1988) each area has its official bodies and specific rules designed to protect the authenticity and quality of the products. These bodies are the *Consejo Regulador de la Denominación de Origen 'Jerez-Xeres-Sherry'*, (Sherry) the *Instituto do Vinho do Porto* (Port) and the *Instituto do Vinho da Madeira* (Madeira), founded in 1934, 1933 and 1979 respectively (Cossart, 1984; Fonseca *et al.*, 1987; González Gordon, 1990). A detailed description of regulation is beyond the scope of this chapter, but where European Union or local rules have a direct effect on production techniques they will be mentioned at appropriate points.

Finally, while recognizing the vital role of viticulture in the style and quality of the final product, we shall restrict our coverage to those aspects of vine growing and grape production which we consider to contribute to the special and unique characters of fortified wines. Again, the reader is referred to many and varied treatises on general viticulture (*e.g.* Foulonneau, 1971; Winkler *et al.*, 1974; Champagnol, 1984; Fregoni, 1985; Coombe and Dry 1988, 1992) and publications covering grape production for fortified wines more specifically (*e.g.* García de Luján (1972), Peman Medina (1972), González Gordon (1990), García de Luján *et al.* (1990), Goswell and Kunkee (1977).

Origins and Current Status of Fortified Wines

The practice of adding alcohol derived from grapes to grape must, partially or wholly fermented by the action of yeasts, to produce a beverage of different style, character and alcoholic strength to that which fermentation of the must alone would give, is at least 300 years old (Goswell and Kunkee, 1977). Traditional fortified wines seem to be associated generally with areas where the climate and soil conditions do not favor the production of grapes suitable for high-quality light wines. Thus where warm or hot climates might produce bland white table wines (the Sherry area of Spain), astringent red wines (the Port area of Portugal), or cooler and damp summers might contribute to wines with an acidic or 'green' character (the islands of Madeira), fortification and the development of associated techniques in maturation and blending were used to produce drinks of great individuality and style. There is also little doubt that, in some cases at least, the practice of spirit addition arose partially to suppress undesirable microbial growth during storage and shipment; in spite of the generally unfavorable environment which they provide for microorganisms, fortified wines themselves are not without their problems of biological stability (see the section "Microbial Spoilage").

An accurate assessment of current global production or consumption of fortified wine is not easy, since wine production statistics often fail to distinguish between fortified and non-fortified products. However, Table 8–1 gives a synopsis of recent sales data, which serves to show that, although apparently declining, the importance in volume terms of fortified wines is still considerable. The high alcoholic strength of liqueur wines normally dictates their consumption either as aperitifs or as dessert wines at the end of a meal.

Outline of the Basic Processes

Figures 8–1 (a), (b) and (c) show generalized flow charts for the production of Port, Sherry and Madeira, which serve to contrast the processes which will be considered in detail later. Although the geographical and legislative constraints in the countries of the European Union preclude the production of these wines outside their respective demarcated areas, winemakers in 'New World' countries might expect to produce more than one style of fortified wine plus several styles of light

Table 8–1 Estimated global sales of fortified wines

	Annual sales (hl)					
Type of wine	*1996*	1997	1998	1999	2000	2001
Sherry	881900	799115	814436	743019	695378	569002
Port	922987	903779	944648	953843	957450	950940
Madeira	36476	37570	38752	36273	40176	47074
Total	1841363	1740464	1797836	1733135	1693004	1567016

Sources: Consejo Regulador de Denominacon de Origem 'Jerez-Xeres-Sherry'
Instituto do Vinho do Porto
Instituto do Vinho da Madeira

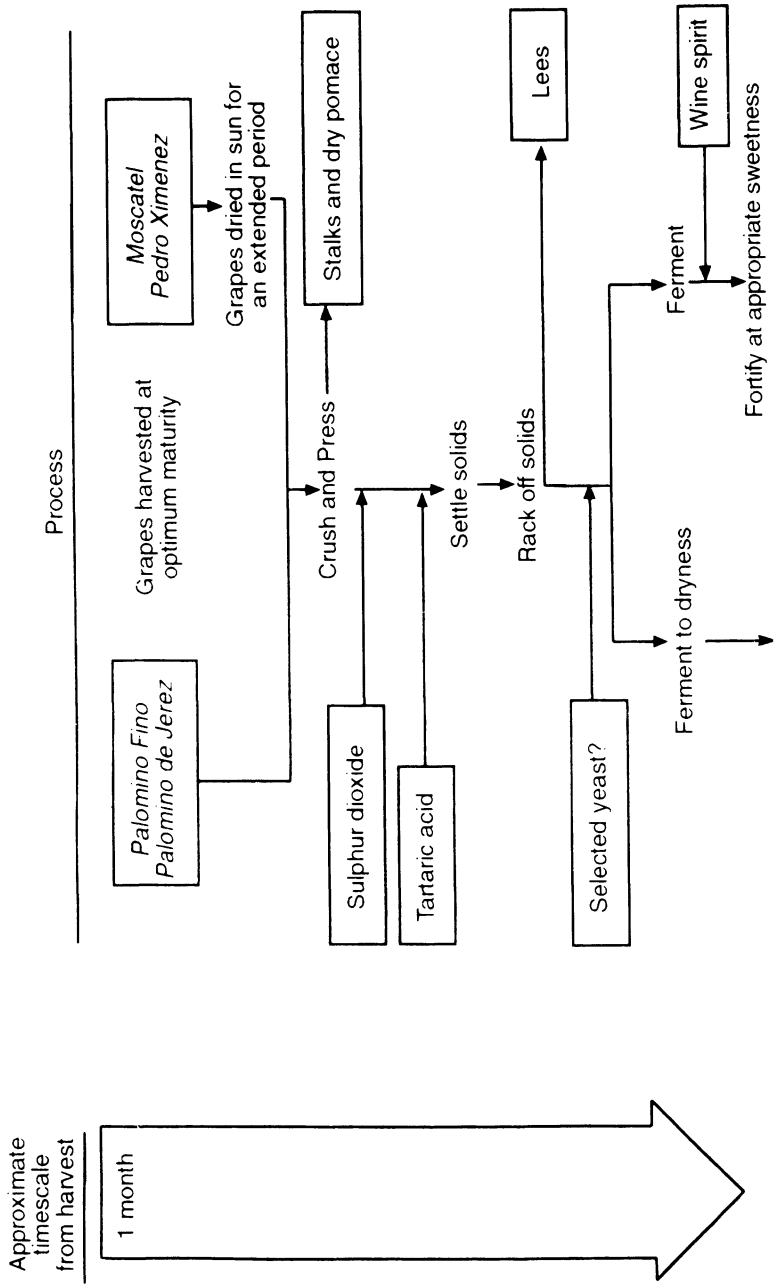
wine on the same premises. Sherry is made exclusively from white grapes, from a limited number of varieties of the vine *Vitis vinifera*. Port may be made from red or white grapes, but these are always vinified and matured separately, to produce red or white wines. Madeira is produced from separately vinified and matured red or white gapes, the maturation process tending to minimize apparent differences in origin. The addition of spirit to raise the alcoholic strength of the products is a common feature of all these wines, but may occur at different stages of their production. Base wines for Sherry are mainly dry, having undergone primary alcoholic fermentation to dryness (*i.e.* less than 2 g l^{-1} residual sugar). Fortification with alcohol, and sweetening with grape-derived products where necessary, are then carried out later in the process. Port receives its fortification during primary alcoholic fermentation, the increase in ethanol concentration effectively terminating yeast activity, and thus the sugar in the final product is entirely residual from the original grape musts. The exact timing of spirit addition is dependent on the style of wine desired, although the majority of wines are fortified after approximately half the original sugar in the must has been consumed. Madeira may be fortified during primary alcoholic fermentation or after this has run its course to dryness. Sweetness may be adjusted later either with concentrated grape must or *surdo*, a sweetening wine.

All three types of wine owe much of their distinctive characters to the aging and blending processes. Base wines for Sherry are relatively bland but develop intense and particular flavors during aging in oak casts (butts), with or without development of *flor*, a surface growth of film-forming yeasts. Young wines destined for red, and to a lesser extent white, Ports have strong grape-associated characters which are modified during maturation but which remain crucial to the quality of the final product. Madeiras are also somewhat dependent on the flavors of the freshly fermented musts, but most wines are subjected to a prolonged heating or *estufagem* (around 3 months at up to 50 °C), which inevitably has great influence on the final product. Blending during maturation is characteristic of these fortified wines, the actual systems used differing between the three areas. Since we consider the blending processes to be critical to final quality, style and stability, we discuss these in detail in the relevant sections.

The requirement generally amongst consumers for bright products, without sediments in the bottle in most cases, means that the majority of the wines considered here are subject to clarification and to some form of stabilization process, generally cold treatment at temperatures below 0 °C, before bottling. Detailed aspects of, and exceptions to, these procedures are discussed at appropriate points later.

ALCOHOLIC FERMENTATION

It is not our intention here to attempt a detailed description of the metabolic events of


Process
Palomino Fino
Palomino de Jerez
Grapes harvested at optimum maturity
Moscatel
Pedro Ximenez
Grapes dried in sun for an extended period
Crush and Press
Stalks and dry pomace
Sulphur dioxide
Tartaric acid
Settle solids
Rack off solids
Lees
Selected yeast?
Ferment to dryness
Ferment
Wine spirit
Fortify at appropriate sweetness
Approximate timescale from harvest
1 month

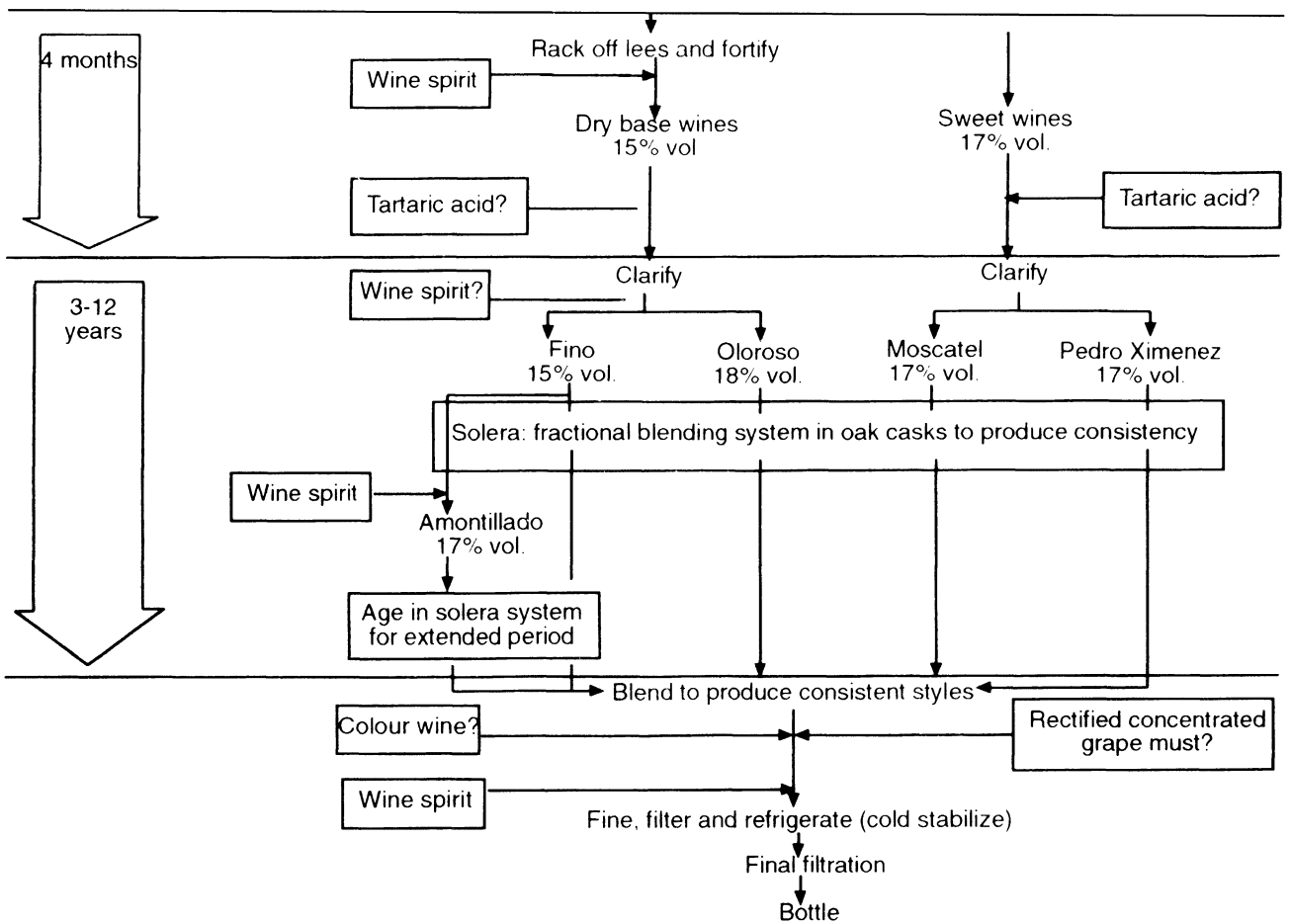
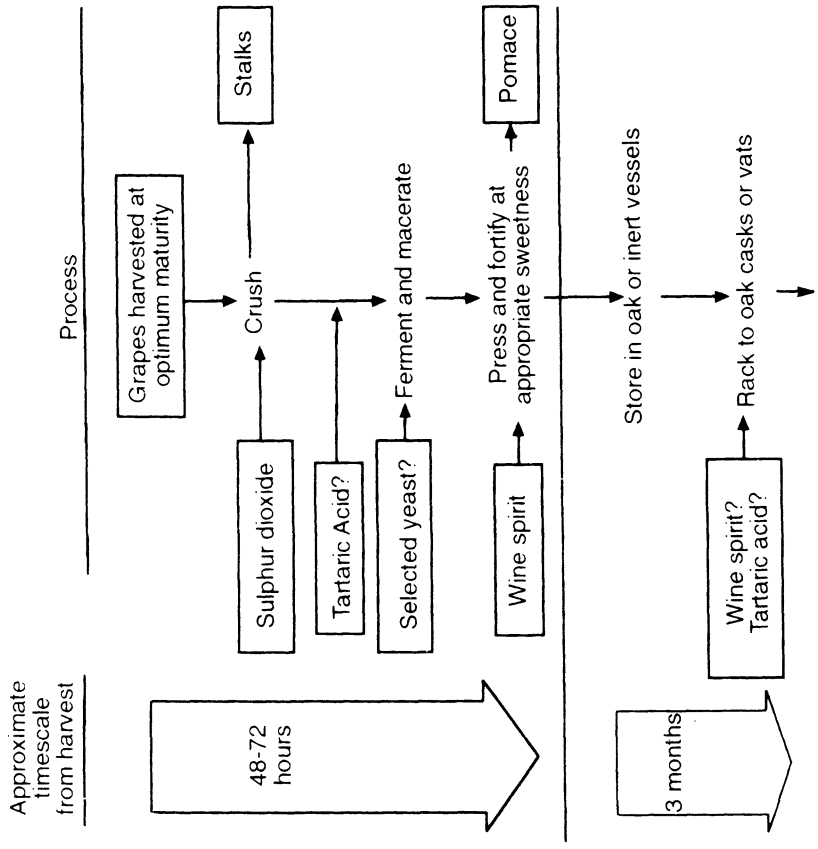


Figure 8–1a Simplified flow chart for the production of sherry.


Process
Approximate timescale from harvest
Grapes harvested at optimum maturity
Crush
Stalks
Sulphur dioxide
Tartaric Acid?
Selected yeast?
Ferment and macerate
Press and fortify at appropriate sweetness
Pomace
Wine spirit
Store in oak or inert vessels
Rack to oak casks or vats
Wine spirit? Tartaric acid?
48-72 hours
3 months

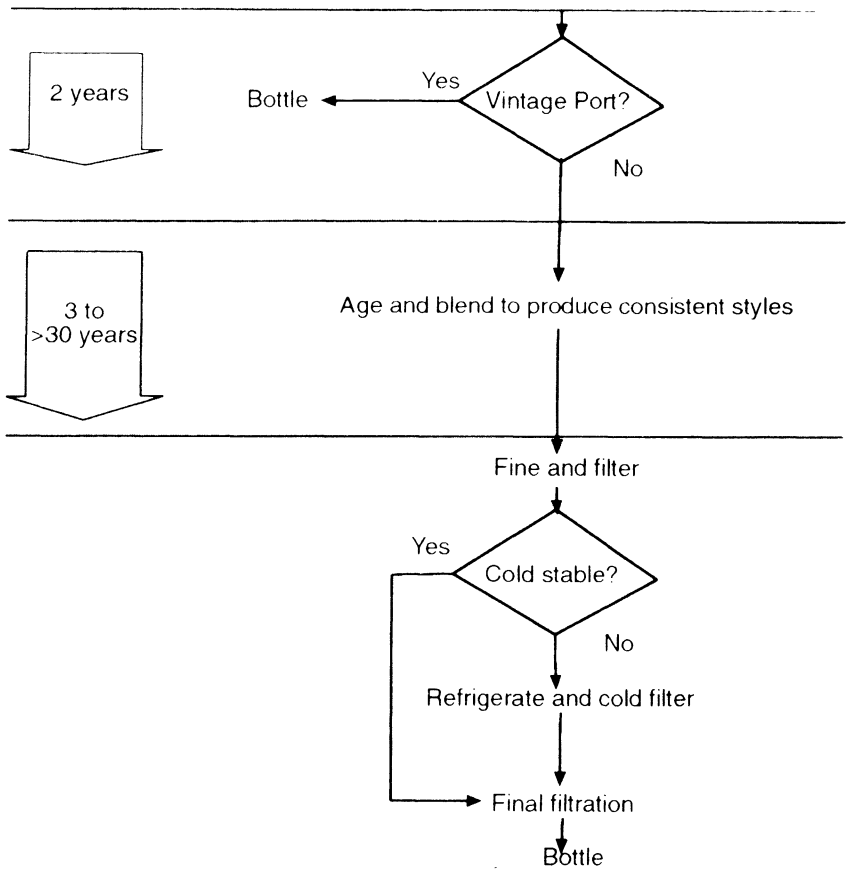
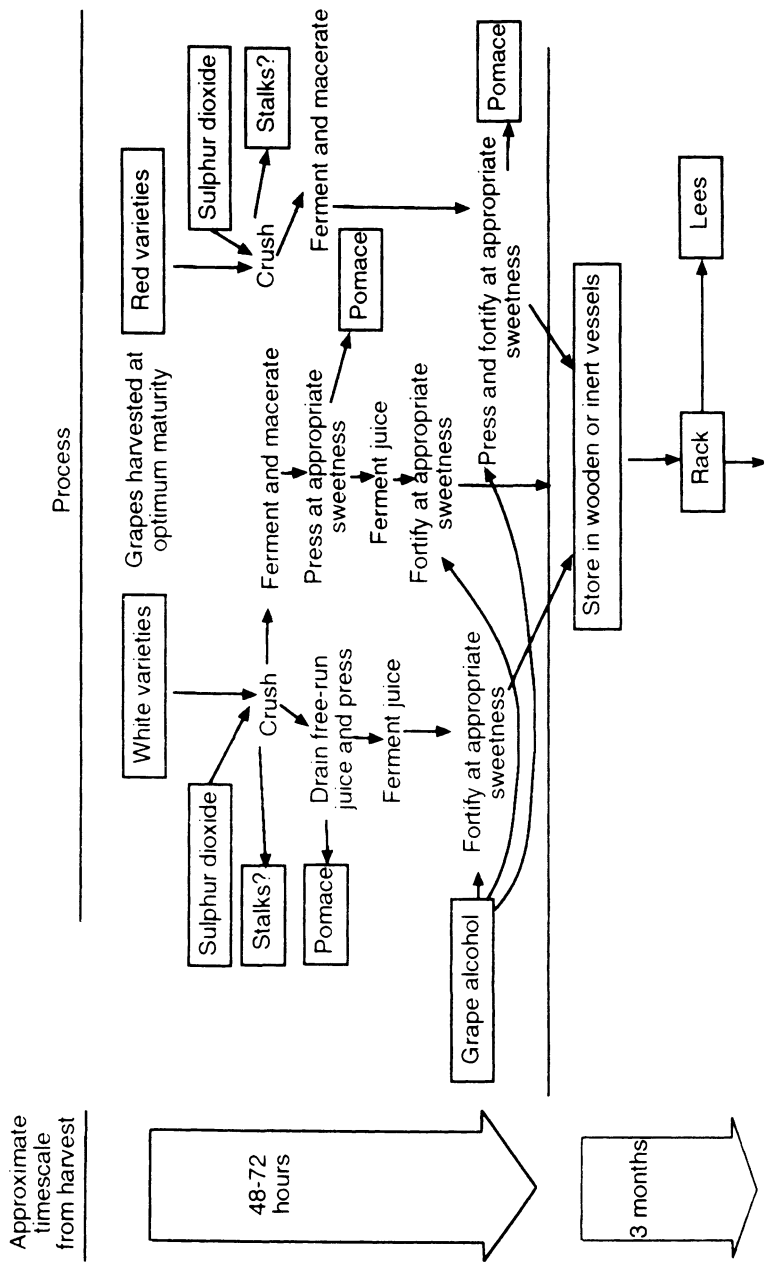


Figure 8–1b Simplified flow chart for the production of port.


Process
Approximate timescale from harvest
48-72 hours
3 months
White varieties
Grapes harvested at optimum maturity
Red varieties
Sulphur dioxide
Stalks?
Pomace
Crush
Drain free-run juice and press
Ferment juice
Ferment and macerate
Press at appropriate sweetness
Ferment juice
Fortify at appropriate sweetness
Grape alcohol
Fortify at appropriate sweetness
Sulphur dioxide
Stalks?
Crush
Ferment and macerate
Pomace
Press and fortify at appropriate sweetness
Pomace
Store in wooden or inert vessels
Rack
Lees

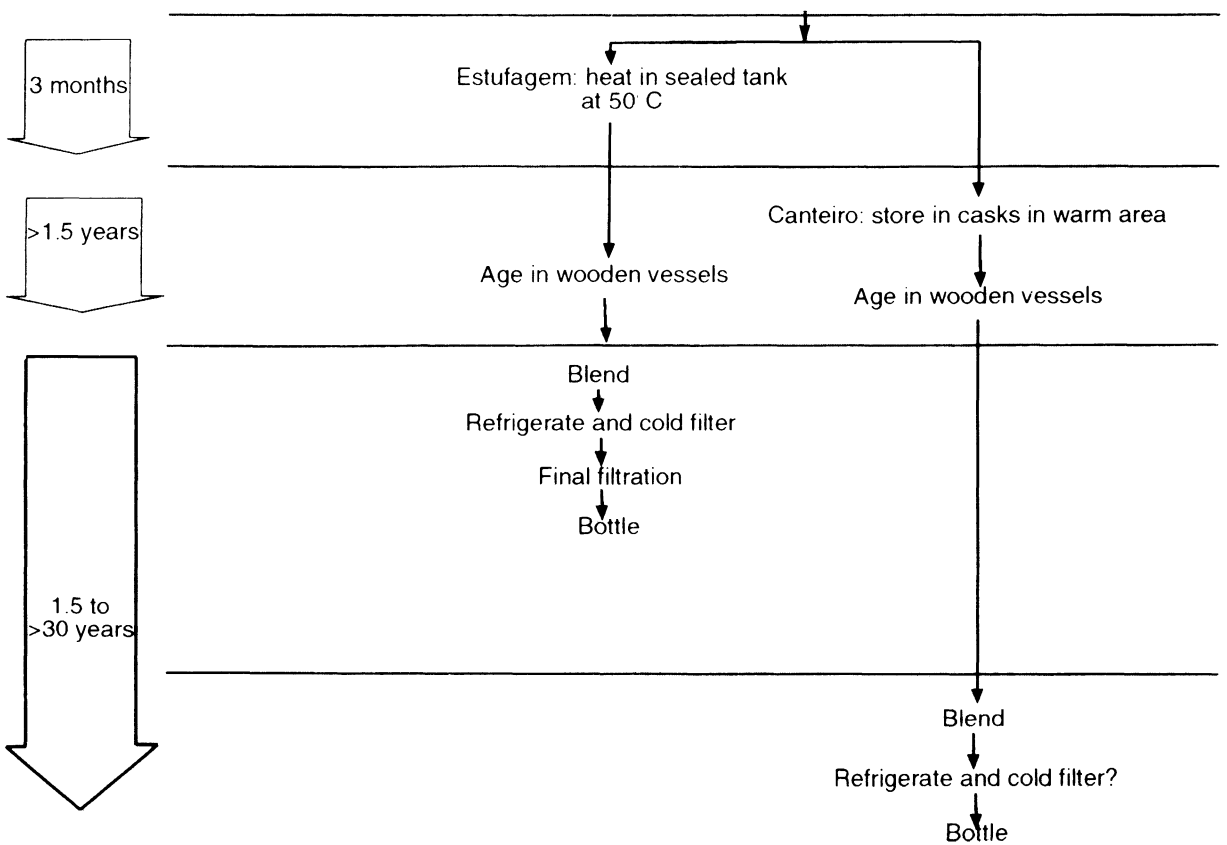


Figure 8–1c Simplified flow chart for the production of Madeira.

alcoholic (primary) fermentation of grape must, since this has been covered more than adequately in recent reviews (Bisson, 1993; Fleet and Heard, 1993; Henschke and Jiranek, 1993; Kunkee and Bisson, 1993; Radler, 1993; Rauhut, 1993). Reliance on indigenous yeasts, either derived from the grapes themselves or from winery equipment, as a source of fermentation organisms for these fortified wines is still considerable, in contrast to many other wine growing areas. This reliance may partly be due to tradition (in Sherry, for instance, commercially produced yeast cultures could interfere with the development and ecology of the *flor* film), and partly to a belief that indigenous yeast strains are particular to a region and contribute to the 'typicity' of the wine. Frézier and Dubourdieu (1992), for example, have demonstrated apparent stable dominance of a particular wild strain of *Saccharomyces cerevisiae* in a winery in the Bordeaux area, but the regional significance of their findings is unclear, and there have been few published quantitative ecological studies in the Sherry, Port or Madeira areas. There seems no reason to suppose that there are great differences in the yeast species active in fermentation from those identified in other areas (reviewed by Fleet and Heard, 1993; Bisson and Kunkee, 1991), *i.e.* growth of *Kloeckera, Hanseniaspora, Candida* and possibly *Pichia* species during the first few days of fermentation followed by a gradual dominance by *S. cerevisiae*, either inoculated or indigenous (García Maiquez, 1982; Goswell and Kunkee, 1977; Valcarcel *et al.*, 1991), Where fermentation is arrested by fortification before alcoholic fermentation has run its course, as is the case with most Ports, some Madeiras, and sweetening wines for Sherry, the influence of non-*Saccaromyces* species on the flavor of the final wine is unclear and merits investigation.

FORTIFICATION SPIRIT

Two types of spirit are used to produce the fortified wines described here. Sherry and Madeira are fortified with nearly neutral spirit of alcoholic strength not less than 96 % vol, continuously distilled from wine or wine-derived products such as less and pomace, whereas Port production uses wine spirit (commonly, though incorrectly, termed "brandy") or 76–78 % vol. The fortification alcohols may be produced from outside the regions of origin of the wines, Sherry alcohol for example coming commonly from the La Mancha area of Spain, and Port spirit from various areas in Portugal and the rest of Europe.

Neutral alcohol makes little direct contribution to the flavor of the product, other than raising the alcoholic strength and affecting flavor thresholds of other components. Wine spirit for Port contains significant levels of higher alcohols, esters and aldehydes which have direct effects on flavor and secondary effects on the maturation of the product (see the section "Basic Styles of Wine" under "Port"). Winemakers in other areas commonly use neutral alcohol for all styles of fortified wine, although there is interest in adding different distillation fractions to neutral spirit to produce different characters in the finished wine (Birks, 1992). In all these wines, a significant part of the volume of the final product is made up of spirit, so concentrations in the latter of, for example, heavy metals and urethane (see the section "Ethyl Carbamate") are of importance.

SHERRY

Definition

Sherry is the name given to a number of related types of dessert wine originally developed in the area around Jerez de la Frontera, in the province of Cadiz, in the south of Spain (Sills, 1988). The materials and methods used in its manufacture are strictly controlled by a committee appointed under the authority of the Spanish Government (Anon, 1977), the *Consejo Regulador*. Sherry is now subject to Council Regulation (EC) N° 4252/88, (1988) on the preparation and marketing of liqueur wines produced in the European Union (García Ruíz, 1991). Minimum acquired alcohol contents are 15 % vol. for dry and medium sherries (*q.v.*) and 15.5 % for cream sherries (Anonymous, 1999).

Viticulture

The Sherry vineyards are situated in a diamond-shaped area with Jerez de la Frontera more or less at the center; a proportion only (105000 ha) of the area is planted with vines. The agreed yield limit of 80 hl of must per ha and 4100 vines per ha (Anonymous, 1977), equivalent to 11500 kg ha^{-1}, should be sufficient to replace the expected annual Sherry shipments.

Climate and Soil

The quality of Sherry is affected by innumerable factors and is a function of the overall climate of the area and the mesoclimate of the vineyards, influenced by factors such as slope, aspect and drainage (García del Barrio, 1979). The best vineyards are situated in the low hills composed of a chalky soil known locally as albariza, most of which occurs in a broad area immediately to the west of Jerez.

This preferred soil is a clay of alkaline pH (7.5–8.5) with a high content of active lime (as much as 70 % calcium carbonate), and other soils consisting of sand, clay, loam and humus (García del Barrio, 1979). Rootstocks resistant to high lime contents must be used (García de Luján *et al.*, 1990). Important to this type of soil are its water absorption and retention properties during the rainy season and dry summer respectively (Goswell and Kunkee, 1977). When wet it has a paste-like consistency and hinders vineyard operations; when the soil dries it reverts to a fine powder, without cracks, reflecting heat and hence protecting the moist ground below.

The climatic character of the Sherry area is strikingly constant (García del Barrio, 1984). There is very little cloud cover (65 days a year). Mean monthly temperatures range from 10.5 °C in winter to 25 °C in summer, and maximum shade temperatures are between 35 °C and 38 °C in July and August. Evaporation is high (*ca* 3 mm per day). Relative humidity, normally between 55 %–70 %, drops to about 30 % and temperatures rise dramatically when the south-easterly *Levante* wind blows; the latter winds are unpopular as they are said to diminish vine yield. However, the predominant cooling south-westerlies (known locally as the *poniente*) from the sea can raise the relative humidity to about 85 %. Rainfall is moderate (about 620 mm per annum) but quite variable. From May until October is a dry period, but rain at the end of September, during the vintage period, is not uncommon. This can be inconvenient for the harvest operation but does not have a deleterious effect on the quality of the resulting wine.

Vineyards and Grape Varieties

Rows of vines are now planted 2.30 meters apart, with the vines spaced about 1.15 meters apart in each row, giving a density of 3775 vines per ha (García de Luján, 1988). This spacing allows cultivation by tractor, and would also permit mechanical harvesting, although as yet no machine is in commercial use.

The vines are always grafted onto American rootstocks resistant to the root aphid *Phylloxera*. Soil analysis determines choice of rootstock as not all varieties are suitable for growing in soil of high calcium carbonate content (Goswell and Kunkee, 1977). Virus free rootstocks are now available (García de Luján *et al.*, 1983), but were not obtainable when many existing vineyards were planted. Grafting material was taken from selected healthy branches of *Palomino* vines.

Whereas at least six white grape varieties were once grown for Sherry (García de Luján *et al.*, 1990), currently only four varieties may be planted: *Palomino de Jerez, Palomino Fino, Moscatel* and *Pedro Ximenez* (Anon., 1977). Of these, little if any *Moscatel* is incorporated as flavoring by the leading Sherry producers. This variety, representing less than 2 % of planting, is concentrated on sandy ground around Chipiona, south of Sanlúcar, where about 280 ha have been planted. *Pedro Ximenez* is used only for sweetening wine and may be obtained from outside the demarcated area (Council Regulation (EC) N° 4252/88, 1988). *Palomino de Jerez* is not currently grown (I.N.D.O., 1980; García de Luján *et al.*, 1990), and for all practical purposes Sherry vineyards are planted with the higher yielding *Palomino Fino*.

Almost all vines are now supported on wires but are still trained low, with one wire at 50 cm above ground level and another at approximately

1 m. Vines are traditionally pruned with two short spurs 30 cm to 40 cm above soil level. The fruiting branch (*vara*) is restricted to 8 buds; the replacement spur to 1 or 2 buds (Peman Medina, 1972; García de Luján *et al.*, 1990). This system is not compatible with mechanical harvesting. Although experiments with higher pruning systems have given apparently favorable results (Mey, 1988), grape damage by harvesting machinery may be prejudicial to wine quality, (García Barroso *et al.*, 1988) particularly in the establishment, growth and metabolism of the *flor* film during maturation (M.D., unpublished results).

Water availability for vines is improved by *aserpia*, whereby a series of square basins is cut on vineyard slopes after the harvest, restricting rainwater flow and reducing soil erosion (González Gordon, 1970). Vineyards in Spain generally are not irrigated, and in Jerez, irrigation is forbidden. Manure (*ca* 45 tonnes per ha) or organic fertilizer is applied every four years; mineral fertilizers are used annually (Goswell and Kunkee, 1977) (*ca* 0–40 units of nitrogen, 60–80 units of phosphate and 40–80 units of potash per ha). Excess nitrogen should be avoided (Peréz Garcia, 1981).

The most important pests and diseases in the area are grape berry moth (*Plychrosis botrana* or *Lobesia botrana*), powdery mildew (*Uncinula necator*) and two-spotted mite (*Tetranychus urticae*). Chlorosis sometimes occurs in Jerez vineyards (González Gordon, 1990). Intensive fertilization and spraying programs are expensive, and form a significant part of grape production costs.

Production in a mature (4–20 year year old) vineyard can be 12.5–16.5 tonnes per ha, before quantities begin to decrease. A vineyard thus has a commercial and profitable life of some 30 years, after which other crops may be planted for a recovery period of a few years (Goswell and Kunkee, 1977).

Vintage

The use of a single grape variety, *Palomino Fino*, on similar soil in a compact area results in very uniform ripening; thus for optimum grape conditions for wine making the harvest must be rapid (three weeks), necessitating considerable labor and equipment. While traditionally the vintage starts in Jerez on September 8th, the exact date varies and is determined primarily by grape maturity. At optimum ripeness (maximum juice and sugar yield) the pips separate easily from the pulp and the bunch stems darken (González Gordon, 1990).

The natural alcoholic strength of Sherry musts may not be less than 10.5 % vol. (Council Regulation (EC) N° 4252/88, 1988). The former practice of drying *Palomino* grapes in the sun for 24–48 hours has been discontinued because of labor costs (Amerine *et al.*, 1980). Grape juices with at least 11.5 % vol. potential alcohol and as little as 2.75 g l^{-1} total titratable acidity (as tartaric acid), are considered satisfactory.

Titratable acidity is not a reliable indicator of acidity in *Palomino* must, where the frequent occurrence of high pH is correlated with high contents of potassium and phenolic compounds. Studies of grape maturity over extended periods have shown that the index ^{0}Brix $\times$ $(pH)^2$ (Coombe *et al.*, 1980) gives a good indication of the quality of the processed product (alcohol, acidity and associated quality factors), with values of 270–295 indicating optimum maturity. Recently prolonged grape maturation studies on different sites and using different analytical parameters, combined with factor analysis have identified three major factors accounting for grape maturation, enabling a more accurate modelling of the maturation process and its optimum point (Palacios *et al.*, 1997). The latter would normally occur between September 10th and 20th, with overmaturity occurring from the beginning of October and bunch rot developing after the middle of this month.

Grape bunches are hand-harvested into plastic boxes or baskets, holding 15–20 kg fruit. For larger wineries transport from the vineyard is by tipper lorry, with the lorry bed (50–60 cm depth) protected by a waterproof tarpaulin or an open polyester tank. Harvesting under these conditions, and transport and crushing within four hours of picking, minimizes both tissue

damage and release of polyphenol oxidase, and has little or no deleterious effect on the resulting wine.

Vinification

Since the first stage of the Sherry process is the production of a dry white wine, involving standard vinification techniques, we will concentrate here on aspects unique or special to Sherry.

Pressing

Methods of pressing and crushing vary depending on the type of equipment available, although the basic principles are similar. Grape bunches are dumped in a hopper and conveyed to a roller crusher by screw conveyor. Stalks are not removed as they are considered to aid draining. After crushing, the must is pumped to the presses. Either batch presses (horizontal mechanical piston or pneumatic) or a continuous process, introduced into the area some 20 years ago (Mey, 1988) are used. The latter normally involves a static predrainer (8 % of total juice yield) followed by an inclined drainer (44 % yield) and two screw dejuicers operating at 1.0 and 2.5 bar respectively (37 % yield). Final pressing is by two continuous screw presses in parallel (11 % yield). Using this system a team of three can process 20 tonnes of fruit per hour, with an overall juice yield of over 800 l per tonne. Although both batch and continuous systems produce good quality juice, the economic advantages of the latter system are considerable. However, since the quality of finished wine is influenced by mechanical treatment of the grapes (García Barrosa *et al.*, 1988), alternative continuous systems have been investigated. One of us (M.D.) (Dominguez) has demonstrated that modern belt presses (Maurer, 1989) have significant advantages in terms of labor, space, energy requirements, premium quality juice yield (61 % of total) and solids content when used with *Palomino* grapes. Juice fractions can be collected independently in stainless steel trays, and waste solids (pomace) can be discharged to continuous screw presses to produce fractions suitable for distillation material. Over 25 tonnes per hour of fruit can be processed. (Maurer, 1989).

Juices should contain less than 1 % w/v solids, and are often cooled (12–15 °C) and settled for 8–18 hours to reduce the load on clarifying centrifuges and rotary vacuum filters. Juice separation techniques influence the browning potential of the finished wine, through the extraction of phenolic precursors of oxidative browning (Singleton and Esau, 1969), and juice fractions are normally separated on the basis of levels of total phenolic compounds. Free-run juice with less than 200 mg l^{-1} total phenolics (expressed in gallic acid equivalents) is kept apart from later press fractions with up to 300,475 and over 500 mg l^{-1}. Fractions from continuous screw presses, with up to 850 mg l^{-1} total phenolics, are not considered suitable for quality Sherry.

Low acidity juices are corrected, normally with tartaric acid, to reduce the pH to below 3.45 (Valcarcel *et al.*, 1991). The practice of adding gypsum ("plastering") to must to reduce its pH through precipitation of calcium tartrate (Goswell and Kunkee, 1977; Benitez *et al.*, 1993) appears to be declining; levels of 1.25–2.22 g l^{-1} are used (Casas Lucas, 1968). Even with these corrections later press fractions may ferment at pH 3.85 or higher.

Sulfur dioxide is adjusted to give 0.5–0.9 mg l^{-1} molecular SO_2, although there is a tendency to restrict its application (Suárez Lepe and Iñigo Leal, 1990). The addition of alcohol up to 3–4 % vol. before fermentation, to select out undesirable yeasts and bacteria, is an alternative to high levels of SO_2, and is considered beneficial (Iñigo Leal, 1976; García Maiquez, 1988).

Fermentation and Fortification

Formerly all fermentation was carried out in oak butts (500 to 600 l) used for aging and shipping wine. Given the small capacity, temperature control was not essential (Goswell and Kunkee, 1977). A limited amount of fermentation is still carried out in casks, to produce characteristically flavored blending wines, to season new casks prior to entering the maturation system and to supply a demand for sherry-matured butts from

Scotch whisky producers (Mey, 1988; González Gordon, 1990). Most wine, however, is fermented in tanks on the same site as the vintage equipment.

Cylindrical stainless steel fermenting tanks normally between 500 and 1000 hl capacity (occasionally up to 4000 hl) are most popular. Temperature control, essential with such large volumes of fermenting juice (Williams, 1980), can be by external water curtain, cooling jacket or heat exchanger; most winemakers regard 25 °C as optimal (Suárez Lepe and Iñigo Leal, 1990).

Many wineries prepare their own yeast starter from a small scale harvest 5–6 days before the main vintage. This starter is used at a rate of 4–5 % vol. in the fermenters (Valcarcel *et al.*, 1991; Suárez Lepe and Iñigo Leal, 1990). Commercial yeasts are not normally used.

In November dry wines with an alcoholic strength of 11–12 % vol. are provisionally classified on the basis of quality. At this stage the conversion of L-malic acid to L-lactic acid by lactic acid bacteria ("malo-lactic fermentation"; see, for example Kunkee, 1974, 1991) has taken place. The skilled producer can predict with remarkable accuracy which of the wines will support substantial *flor* growth to become *finos* or *amontillados*. The coarser wines are destined for *olorosos* or *rayas*.

After this first selection the wines are racked, and the decanted wine fortified to 15.5 % vol. Coarse centrifugal clarifiers are used in some wineries to speed up this process. The fermentation lees represent, on average, 4–8 % vol. of the fermented juice; wine recovered from lees by rotary vacuum or press filer can be fortified to 18.5 % vol. and marked as *raya*.

Before the alcohol is used it is mixed with an equal quantity of wine and allowed to settle for about three days. This product when used for fortification causes less clouding than would the addition of unblended alcohol (González Gordon, 1935).

Styles of Wine

Unblended sherries at this stage are divided into two main groups: *finos* and *olorosos*. This classification is subject to refinement and modification as the wines develop. The criteria used by the taster at this first selection vary from producer to producer, and have an important influence on house style.

Finos, derived mainly from free run juice (less than 200 mg l^{-1} total phenolics) are pale and dry. They must be free of signs of bacterial spoilage, and sufficiently full to sustain losses of "body" inherent in *flor* maturation (Casas Lucas, 1985). Volatile acidity, as acetic acid, should be around 0.2–0.5 g l^{-1}.

Olorosos have a clean nose and strong bouquet, but a less pungent aroma than *finos*. They are full-bodied, more vinous, and coming mainly from wines with higher levels of total phenolics (up to 475 mg l^{-1}), are usually darker. They are less likely to develop a spontaneous *flor* film, and indeed are refortified to 18.5 % vol. alcohol to prevent this. Voltile acidity is usually higher (0.7–0.9 g l^{-1}) than *finos* (García Maiquez, 1988).

These two fundamental styles are themselves divided into several sub-varieties (González Gordon, 1990). *Raya* wines belong to the *oloroso* group, but are of lower quality. They are made mainly from highest tannin press fractions (over 550 mg l^{21} total phenolics) and benefit from exposure to higher temperatures: often they are stored outdoors in the sun. This is an economical way of heating, although wine losses by evaporation are substantial (Pérez Rodríguez, 1983). *Rayas* are usually blended in small proportions with *olorosos* and may eventually develop into darker *olorosos*. At the first selection alcoholic strength is adjusted to 18.5 % vol. At one time wines affected by acetic acid bacteria might have been blended into *rayas*, but modern vinification has effectively eliminated these bacterial problems (Mey, 1988).

Aging and Maturation

The original method of maturing Sherry (the *añada* system), keeping wines from different vintages separate until they were ready for use (González Gordon, 1935), now forms the first stage of aging. The young wines are allowed to mature unblended for about a year. After a sec-

ond selection, Sherry will then enter a dynamic and continuous fractional blending process called the *solera* system, which provides consistency of quality and character.

Cellars

Sherries are matured in tall (12 m), well-ventilated buildings (18.5 liters of air per liter of stored wine), locally called *bodegas*, where extremes of temperature are avoided without the need for air-conditioning. *Bodegas* are normally west-facing to catch cooling winds, particularly desirable within 2 m of the floor. The latter should be soft to protect rolling butts and porous to maintain uniform temperature and humidity (above 60 %). The humidity is kept stable by frequent watering.

The oak butts (500–600 l) are stacked in long rows, up to five high, with the *finos* on the cooler lower levels, and the *olorosos* in the upper rows.

The Solera *System*

Detailed descriptions of the characteristics of and operations of the *solera* system have been given by several authors (Casas Lucas, 1968; González Gordon, 1990; Goswell and Kunkee, 1977; Mey, 1988). The system is basically a progressive topping up of older casks from younger wines of the same style, so that the wine is continuously blended, and emerges with a consistent character. The frequency of transfers, and the maximum amount of wine removed from each cask at one time, varies according to the producer, as does the number of stages (*criaderas*) in each *solera* system. *Finos* need the most *criaderas*, being most susceptible to changes of style, and should be carefully managed up to the last stage of the *solera* system; this last stage being appropriately termed a *solera*. The *solera* and the various *criaderas* are not necessarily kept next to each other and may even be in separate *bodegas* when space is short. We shall refer to the complete system of *criaderas* and *solera* as the "*solera* system" and the last stage simply as the "*solera*".

The required volume of wine for a shipping blend is removed from the *solera* stage, and will contain an equal contribution from each of the constituent casks. The same volume of wine is removed from the constituent butts of the *1st criadera* and, after blending in a tank, is used to replenished the *solera* stage. The *1st criadera* is replenished with wine from the *2nd criadera*, which in turn receives wine from the *3rd criadera*, and so on, the final *criadera* being replenished by *añada* wine of suitable style. This wine is chosen from casks in the *añada* on their individual merits after tasting and analysis. Fixed pipelines may facilitate the frequent movement of wine through the system, but the procedure remains labor intensive and contributes substantially to wine costs.

The nature of the *solera* system makes it difficult to establish the age of the wine at any stage (the required minimum age for Sherry is three years (Anonymous, 1977)), although the average age can be estimated mathematically (Williams, 1980; Pérez Rodríguez, 1989). It has been calculated that after 12 years aging wine losses by ullage would overtake the increase in value of the wine (Collado Casal, 1983). A *solera* system, with up to five or more *criaderas*, each having several hundred casks, can thus contain well over 1000 butts, and represent a considerable burden on a producer's assets.

The *solera* system is crucial to the production of all Sherry. Careful management of a system allows variations in style to be corrected during aging, so that a consistent volumetric mixture of wines from different *soleras* will result in a consistent end product.

Aging Under Flor

Wines destined for *finos* will, under the right conditions, develop spontaneously an unsightly wrinkled film of yeast (*velo de flor*) at the air/wine interface. Flotation of the yeast may be connected with the synthesis of hydrophobic cell surface proteins (Martinez *et al.*, 1997). *Flor* regulates access of air to the wine and prevents growth of spoilage bacteria, and *finos* are thus matured under predominantly anaerobic conditions. Oxidative browning is negligible, and indeed darker wines can be bleached by *flor* maturation (Fornachon, 1972). The *flor* activity fluctuates seasonally, with a peak between February

and June, and a decline to October/November, when the cycle restarts (Dominguez, 1993*a*; García Maiquez, 1988; Lozano and Peridgones, 1991).

Selection of a suitable *añada* wine is critical to *fino* production. Various authors have discussed the influence of base wine composition on *flor* yeast activity (Casas Lucas, 1968; Fornachon, 1972; García Maiquez, 1988; Goswell and Kunkee, 1977; Mey, 1988; Suárez Lepe and Iñigo Leal, 1990). Table 8–2 shows a composition for *añada* wine, based on a synopsis of their recommendations. Pantothenate is important to film growth, and certain amino acids, while of less importance in the establishment of the film, are essential to its maintenance. L-lactate up to a concentration of 3 g l^{-1} is also beneficial to *flor* film maintenance (Suárez Lepe and Iñigo Leal, 1990).

There is some debate as to the origin of *flor* yeasts: whether they are the yeasts responsible for alcoholic fermentation, adapting to the conditions of the aging wine (Goswell and Kunkee, 1977; Amerine *et al.*, 1980), or different strains or species present in low numbers in the wine at the end of fermentation (García Maiquez, 1988; Suárez Lepe and Iñigo Leal, 1990). Equally debated is their taxonomy. Yeasts suitable for production of *flor* films are apparently physiologically different from those predominating in alcoholic fermentation, and various workers have isolated and identified strains which were considered to represent a variety of species, including *Saccaromyces beticus* and *cheresiensis*, both now synonomous with *S. cerevisiae, S. montuliensis*, now considered *Torulaspora delbreuckii* and *S. rouxii*, now included in *Zygosaccharomyces rouxii* (Kreger-van Rij, 1984; Barnett *et al.*, 1990); these studies and others showed that *S. beticus* is the dominant organism in younger wines, diminishing as the age of the *solera* system increases, when *S. montuliensis* becomes more predominant. *S. cheresiensis* is irregular in its frequency and *Z. rouxii* only sporadic (Prostosserdov and Africkian, 1933; Iñigo Leal *et al.*, 1963; Iñigo Leal and Arroyo Varela, 1964; Fornachon, 1972; Suárez Lepe and Iñigo Leal, 1990). More recent studies involving nuclear and mitochondrial DNA analysis of *flor* yeasts has indicated that most populations are made up of closely related strains of *S. cerevisiae*, with a single-strain predominance in individual barrels (Ibeas *et al.*, 1997b).

The development of *flor* is temperature-sensitive, cell growth only occurring between 13 and 25 °C, with maximum proliferation at 22–25 °C. The optimum temperature for *flor* character is considered to be 17–20 °C (Suárez Lepe and Iñigo Leal, 1990; Dominguez, 1993*a*). In Jerez the thickness of the film declines in summer in spite of attempts to regulate temperature and humidity of the *bodega* (Lozano and Perdigones, 1991). This effect seems at least partially to be due to the formation of respiratory defficient mutants at higher temperatures (Ibeas *et al.*, 1997a). A film thickness of 3 to 6 mm is considered ideal, the oxygen status in the *flor* influencing the crucial aldehyde concentration in the wine (Fornachon, 1972; Suárez Lepe and Iñigo Leal, 1990; Dominguez, 1993*a*).

The casks are kept about 80 % full, to maintain a high surface/volume ratio of 17–18.5 cm^2 l^{-1} of wine (Fornachon, 1972; García Maiquez, 1988; González Gordon, 1990). Free access to air should be maintained, and the film should be disturbed as little as possible, particularly during transfers. Movements of 25 % of the wine in

Table 8–2 Suitable *añada* base wine characteristics for *flor* maturation[a]

Alcohol (% vol.)	14.8–15.3
Glycerol (g/l)	6.7–7.2
Fermentable sugar (g/l)	<1.5
Gluconic acid (g/l)	<0.6
Acetic acid (g/l)	<0.65
Malic acid (g/l)	<0.15
Lactic acid (g/l)	<1.15
Total phenolic compounds (mg/l)	<250
Total sulphur dioxide (mg/l)	<75
pH	3.00–3.25

[a]For references see text.

each cask every 90 days have been recommended (Pérez Rodríguez, 1989; Suárez Lepe and Iñigo Leal, 1990). The seasonal nature of the Sherry trade means that in practice these regular movements are not easy to achieve. If larger volumes of wine are moved with less frequency the *flor* film declines through lack of oxygen. It has been demonstrated that the oxygen dissolved in the wine and that in the cask headspace is effectively depleted within a few days of movement. Oxygen uptake of between 3.5 and 5.5 mg l^{-1} should be obtained during movements (Fornachon, 1972; Pérez Rodríguez, 1983; Lozano and Perdigones, 1991; Dominguez, 1993*a*). As well as oxygenation effects, transfers in a *flor solera* system are important to replenish micronutrients, vitamins and growth factors for film maintenance (Casas Lucas, 1985).

The influence of *flor* on the wine is great, and determines the character of *fino* Sherry and *manzanilla*, the dry *fino* style produced in the specific microclimatic conditions found in Sanlúcar de Barrameda (Mey, 1988). The major biochemical changes in the wine through the *solera* system are a slow but measurable decrease in volatile acidity, a gradual reduction in glycerol content, consumption of alcohol as a carbon source (Casas Lucas, 1968; García Maiquez, 1988; Suárez Lepe and Iñigo Leal, 1990), and a pronounced increase in acetaldehyde, normally to around 260–360 mg l^{-1}. Wines with acetaldehyde levels as high as 750 mg l^{-1} can be obtained, but are unpleasant to drink through the dominance of the aldehyde character. The acetaldehyde is believed to originate exclusively from ethanol by enzyme activity (Fernandez *et al.*, 1972; García Maiquez, 1988), and is a precursor for compounds such as acetoin, diethyl acetal and polyphenolic-derived compounds combined with acetaldehyde (Fornachon, 1972; Casas Lucas, 1985). Sporulation and autolysis occur in the yeast-derived sediment in the bottom of the cask, probably also contributing to flavor. In addition to consumption of ethanol by yeast alcohol dehydrogenase, there is an evaporative loss of alcohol of at least 0.2–0.3 % vol. annually which is significant economically (García Maiquez, 1988; González Gordon, 1990; Suárez Lepe and Iñigo Leal, 1990).

While conditions in the film are strongly oxidative the wine below the film is under reducing conditions. Redox potentials vary from 300–320 mV at the bottom of the cask to 340–360 mV nearer the surface. Wines with little *flor* growth will have a redox potential above 420 mV.

Specific wine transfer techniques have been adopted in view of the crucial role of transfers in maintenance of the *flor* film. Wine is drawn from the casks via a small diameter rigid plastic or stainless steel tube, inserted well below the film and adjusted to the final desired level of wine. 6–8 of these siphons are connected by a manifold to a centrifugal pump, and a steady flow of wine is transferred to a temporary holding tank, where it can be homogenized and oxygenated.

Another pump and similar manifold system, with a set of sprinklers, is used to move the wine to the next stage of the system. The sprinklers, made from the same tubing as the syphons, are perforated in the lower half to allow the fresh wine to spray gently and slowly beneath the film and well above the lees. A battery operated sensor shuts each sprinkler tube at a preset wine level to avoid overfilling.

Maturation without Flor

Wine in a *fino solera* system when not regularly refreshed or of considerable age begins to lose its *flor* fim, which may even disappear. Reactions such as esterification and oxidation of aldehydes begin to predominate the aging, and a full-bodied wine known as an *amontillado-fino* (Casas Lucas, 1985) gradually results. This wine can be further aged to produce the style known as *amontillado*.

Refortification to 17.0–17.5 % vol. is usual, both to protect against acetic acid bacteria and to terminate any further *flor* development, and to produce a genuine *amontillado* the wine is aged in a second *solera* system. Here the color continues its change from the straw hues of the *amon-*

tillado-fino to amber and dark gold, and is associated with development of complex nutty flavors derived from the compound maturation. (González Gordon, 1990). The finished *amontillado* can be consumed in its own right or used for complex blends.

The transformation of a *fino* to an *amontillado* takes at least 8 years. An old *amontillado* Sherry may have passed through two or three *fino solera* systems, where the number of stages may be as many as 18–21 *criaderas*, followed by 5–8 *amontillado criaderas* and an *amontillado solera*. Thus genuine *amontillado* Sherry must inevitably be very expensive owing to the enormous amount of time and manipulation required for its production.

Oloroso Sherries are produced from *añada* wines judged not suitable for *fino*, including wines made from later press fractions. After fortification to 18.5 % vol. (thus preventing *flor* growth) the wines are matured under largely oxidative conditions, often in warmer parts of the *bodega*. Although oloroso is a dry wine, glycerol from alcoholic fermentation (7–8 g l^{-1}) gives an impression of sweetness, in contrast to the dry finish of *amontillado*. The color of *oloroso*, initially only slightly darker than a *fino*, rapidly grows deeper and browner with age to a dark amber or mahogany.

In *amontillado* and *oloroso soleras* the casks are kept about 95 % full, lightly stoppered with corks or bungs; average losses by evaporation can be as much as 5 % annually (González Gordon, 1990). Evaporation can take place through the wood (Pérez Rodríguez, 1983), and low humidity in the *bodega* can cause a preferential loss of water molecules, and thus an increase in alcoholic strength. Water loss through evaporation, extraction of compounds from wood and oxidative reactions tend to increase the concentration of non-volatile compounds (Estrella *et al.*, 1985), and fusel oils. Total fusel oil concentration has been shown to increase by over 74 % after more than 43 years of maturation without *flor* (Pérez Rodríguez, 1979). Volatile acidity and ethyl actetate also increase, both by concentration and oxidation and esterification.

A fine *oloroso* requires, as *amontillado*, a long (7–8 year) maturation in wooden casks (García Maiquez, 1988). As with *flor* wines, aging takes at least three years, but transfers may be at six monthly intervals through perhaps three *criaderas* and a *solera*, transferring a little less than 50 % of each cask on each occasion. The frequency and volume of transfers and the size of the *solera* system depend on the *bodega's* strategy.

Sweetening and Color Wines

Sweetening and color wines are fortified at the onset of fermentation (less than 2 % vol. alcohol) to retain most of the grape sugar. Some analytical characteristics of these wines are shown in Table 8–3.

Mistela or *dulce corriente* is made from *Palomino* grapes, and uses only the free-run juice and the first pressing. The unfermented juice is blended with alcohol to about 15 % vol., and the material is often allowed to fall bright when, after racking and fining, a second fortification, up to 17.0–18.0 % vol., takes place. The product may be aged, but, unusually for a constituent of Sherry, without entering a *solera* system. The relatively low sugar content of this wine limits its use as a sweetening agent.

Dulce pasa is made from *Palomino fino* grapes in the Sherry area, by drying bunches in the sun for about two weeks, until the specific gravity (20 ° at 20 °C) of the juice exceeds 1.130. The juice is fortified to about 17.5 % vol. alcohol, and the resultant wine is matured in a *solera* system, where the color deepens from its initial pale gold, and fruity raisin-like flavors develop. *Dulce pasa* has been used increasingly recently as an economical alternative to the classic sweet wine *Pedro Ximenez* (Mey, 1988).

Pedro Ximenez is made exclusively from sun-dried *Pedro Ximenez* (*PX*) grapes. *PX* has been made traditionally with grapes from the hotter district of Montilla Moriles, in the province of Córdoba, this practice being permitted by the *Consejo Reguladór* (Council Regulation (EC) No 4252/88, 1988). The naturally sweet (S.G. 1.105–1.110) grapes are picked around the 10th Septem-

Table 8–3 Typical characteristics of Sherry sweetening and coloring wines

Type of wine	*Acquired alcohol (% vol.)*	*Specific gravity (20°/20°C)*	*Volatile acidity (g/l acetic acid)*	*pH*	*Total phenolics (mg/l)*	*HMF (mg/l)*
Mistella (dulce corriente)	17.0–18.0	1.063	N/A	3.70–3.80	525–625	5–10
Dulce pasa	18.0	1.122	N/A	N/A	N/A	N/A
Pedro Ximenez	17.5–19.5	N/A	>0.60	3.90–4.55	1000–1200	50–75
Moscatel pasa	17.0	1.118	<0.75	3.05–4.25	650–800	20–30
Dulce branco	17.0	1.133	N/A	N/A	N/A	N/A
Rectified Concentrated Grape Must	N/A	1.240	N/A	3.00–4.50	240[a]	10[a]
Color wine	15.0–17.0	1.090	>1.25	3.60–3.80	>5500	3500

Data from Dominguez (1993d)
[a]mg kg^{-1}

ber, and dried on straw mats in the sun (*soleo* process) for 10–20 days before crushing. Bunches are turned periodically to assist even raisining and covered at night to protect against damp. Above juice S.G. of 1.190–1.210 characteristic color and flavors develop (Dominguez, 1993*c*), although juice S.G. up to 1.235 can be reached.

Yield is poor (250–300 l per tonne), and the vinification process slow and difficult to automate. Small horizontal batch presses are used, usually followed by an hydraulic pressing. The expressed juice is extremely sweet and dark, with a pronounced raisin flavor, and is fortified with clean alcohol to 8–10 % vol. and S.G. 1.170–1.175. After 2–3 months the wine is racked, fortified to 17.5–18.0 % vol. and fined. Much of this wine is subject to oxidative maturation in a typical *solera* system, and both the immature product and the matured wine have characteristic rich and raisiny flavors essential to cream sherry blends. Measurable analytical differences during maturation of these wines are slight, and the role of the taster in selecting blending material is important. Finished wines contain about 1.7 g l^{-1} L-malic acid; *PX* grapes generally contain more malic acid than *Palomino fino* (Casas Lucas, 1968). 5-hydroxymethylfurfural (HMF) is derived from fructose and its presence in significant amounts can be indicative of blending with reduced must or caramel or of madeirization (Williams *et al.*, 1983). In *PX* the heating of grape fructose in the acid solution of grape juice is the source of the levels of HMF shown in Table 8–3. The viscosity of these wines reduces absorption by wood, and hence swelling, and can give rise to troublesome leakage from casks.

Moscatel paso is made using similar techniques to *PX*, though with less sun drying, using *Moscatel de Alejandia* grapes, or, prior to its disappearance from the region, *Moscatel morisco*. These wines have a pronounced varietal aroma and are used judiciously in some specialist blends.

Dulce blanco is normally a blend of wine spirit, young *fino* and rectified concentrated grape must (*q.v.*) and has many applications in blending, having little flavor or color of its own. It is thus particularly useful in pale cream Sherries, and for adjusting the sweetness of delicate *finos* without appreciably altering their flavor.

Preparation with alcohol protects against spoilage by xerotolerant (osmophylic) yeasts during storage. Rectified concentrated grape must (RCGM) has itself become widely used in Sherry (Council Regulation (EC) No. 4252/88 (1988)). RCGM is virtually color and odorless, and the low HMF values shown in Table 8–3 are indicative of good processing technology (Saboye, 1981; Dupuy, 1984).

The color of a final blend can be adjusted with color wine, which imparts its own flavor and character to a blend. Color wine is usually ob-

tained by fermenting fresh must to which about two parts of concentrated must (*sancocho*) are added. Musts from the last pressing from *Palomino* grapes, from other grape varieties or from grapes grown on low quality soil are typically used. *Sancocho* is produced by direct heating of must to give a dark, highly caramelized liquid with a specific gravity of about 1.240; further concentration, to S.G. 1.265–1.295 gives *arrope*. These concentrates are added slowly to actively fermenting fresh must in quantities which just allow fermentation to continue slowly to about 8 % vol. alcohol. After 3–4 months the wine is racked and fortified to about 15.0–17.0 % vol. This, premium quality color wine, is known as *color macetilla* (Mey, 1988) and is aromatic, dark, and develops complex flavors, an astrigent dry aftertaste after aging in an oxidative *solera* system.

If the *arrope* is blended with fully fermented must the blend is generally called *color remendado* or *color corriente*, a cheaper, more common color wine of inferior quality.

Commercial Styles of Sherry

About 60 % of total Sherry sales are considered *vino generoso de licor* as defined in "Definition and Scope" with an alcoholic strength of at least 15.0 % vol. and 17.5 % vol. as minimum total alcohol content. *Fino* sherries are usually marketed unsweetened at strengths between 15.5 % and 17.0 % vol., after three to eight years maturation. Wines matured without *flor* (*olorosos* and *amontillados*) are normally sold at 17.0–17.5 % vol. alcohol, or at 19.5 % vol. in the case of old *amontillados*. The finer and older wines may be consumed unsweetened, but the vast majority are sweetened.

Those wines marketed as medium dry, medium, cream or pale cream Sherries, depending on the amount and type of sweetening material added, usually contain predominantly *oloroso* wine, some *fino* to lighten the color and flavor, and, generally small proportions of *amontillado*. *PX* wines and color wines are often used in judicious amounts to improve the roundness and flavor of the blend. Thus the whole range of dry (less than 4.5 % reducing sugar), medium (4.5 %–11.5 % reducing sugar) and cream (11.5–14.0 % reducing sugar) sherries can be made by blending wines from various *soleras*. Of vital importance to the style of the commercial brand is the final blend, and the role of the skilled taster.

Final Processing

Having produced a final blend of a particular style, the Sherry shipper is now faced with the necessity of clarifying and stabilizing the wine to ensure that the bottled product remains free from unsightly deposits associated with potassium bitartrate, polyphenolic and proteinaceous material, and colloidal hazes. Particular attention is required with sweeter and darker wines because of the interfering effects on potassium bitartrate solubility of polysaccharides, proteins and other macromolecules deriving from color and sweetening wines, and the instability of these macromolecules themselves. This complex matrix can also present problems of low flux rates and fouling of filters, particularly where membranes are involved.

The blending process itself may also complicate processing, in that the mixture of two or more elements which have reached a relatively stable equilibrium through aging may give a product which is far from that equilibrium, particularly in the balance between the associated and dissociated forms of tartrate species, and possible complexes of these with other wine components. *PX* wine, for example, can contain particularly high levels of potassium bitartrate and polyphenols. The practice of making up a blend some months before shipment, ostensibly to allow its constituents to "marry", has therefore important implications in stability, in that it allows equilibria to be reached, and unstable products to precipitate, or to reach a form where they will be precipitable in refrigeration prior to bottling (Neradt, 1983).

Most shipping blends will receive a protein-based fining (traditionally egg white, but more

commonly nowadays casein, gelatine, or isinglass) for physical clarification and precipitation of polyphenolic material, followed by filtration, sometimes preceded by centrifugation to accelerate the separation of solids. Bentonite fining may also be used, to attempt to remove unstable protein-polysaccharide complexes, these pre-refrigeration treatments being desirable to remove inhibitors of potassium bitartrate crystallization, which otherwise would not occur to the necessary extent during cold treatment.

Wine is cooled by a plate heat exchanger followed by an ultracooler, and held in refrigerated ranks at -8 ° to -9 °C for 10–14 days, sometimes with the addition of finely ground potassium bitartrate crystals to aid nucleation. The potassium bitartrate can be remilled and reused, although with progressive loss of efficiency (García-Ruíz *et al.*, 1995). After the holding period conventional diatomaceous earth filtration is used to remove the precipitated matter. As in many other wine producing areas, continuous stabilization methods have been evaluated (García-Ruíz *et al.*, 1991). Final pre-bottling filtration is by membrane, the lower strength sherries requiring cartridges of 1.2 μ pore size to ensure microbiological stability although some care should be exercised to avoid removing further stable crystallization inhibitors. During all these processing movements *fino* sherries particularly demand careful handling to avoid future browning problems, and bottling and corking under inert gas has advantages.

PORT

Regulation

The regulation of the production and sale of Port is controlled by two bodies: the *Instituto do Vinho do Porto* (IVP), a government body, and the *Comissão Interprofisional da Região Dermarcada do Douro* (CIRDD), an interprofessional organization with representation of farmers, shippers, and the increasing number of producer-bottlers based in the vineyard area. The IVP is responsible for quality control of fortification spirit, ensuring that wines meet certain minimum organoleptic and analytical standards, research and development, and the establishment of shipping quotas designed to ensure that finished wines are sold with adequate minimum average ages, as well as the attribution of the denomination of origin, generic promotion of the sector, and defense of the authenticity of Port. The CIRDD, amongst other functions, is responsible for vineyard classification (see section 5.2), the annual overall authorization of production of base wines destined for Port, and distribution of this authorization amongst growers.

Geographical Origin

Port is made from red or white grapes produced in or around the upper valley of the River Douro, in northern Portugal. The area in which grapes for Port must be produced and vinified constitutes the world's oldest demarcated wine area, the original definition and marking dating from 1761 (Fonseca *et al.*, 1987). The area as presently defined covers some 250 000 ha, following the course of the Douro upwards from near Barqueiros, some 65 km east of the city of Oporto, to the Spanish border near Freixo de Espada à Cinta, some 170 km from the coast, and extending up to 35 km north and south of the river. Wines must be aged either within this area or in Vila Nova de Gaia, the city opposite Oporto on the mouth of the Douro, in an entrepôt of approximately 15 km^2, in order to qualify for a Certificate of Origin from the *Instituto do Vinho do Porto*. The demarcated area is divided into three sub-regions: the *Baixo Corgo* (west of the Corgo River, which enters the Douro near the city of Régua), the *Cima Corgo* (east of the Corgo River, following the Douro upstream for about 45 km) and the *Douro Superior*, the largest sub-region, surrounding the *Cima Corgo* on three sides, and extending east to the Spanish border. Whereas the *Baixo Corgo* and to a lesser extent the *Cima Corgo*, are densely planted with vines, large areas of the *Douro Superior* remain uncultivated.

The demarcated area is made up of deep river valleys and steep hillsides, particularly in the western and central parts, with rolling high plateaux further east. The soil types considered most favorable for Port grapes are of shistous origin with a high stone content, and predominate on the slopes leading down to the Douro or its tributaries, and on the rolling land in the east. Above about 450 m and in some river gorges the soils are granitic, but these areas, either because of soil type or altitude, are considered to produce grapes unsuitable for Port. Annual rainfall varies from over 1000 mm at the western extremity of the region to 400 mm in the east, and growing season daytime temperatures range similarly from moderate in the west, to the hot eastern valleys (Ramos, 1986).

The climate thus changes from Atlantic in the lower areas of the Douro valley to Mediterranean in the *Douro Superior* (Fonseca *et al.*, 1987); this, together with viticultural practices, has an important influence on wine quality.

Viticulture

Grapes intended for Port production are produced from vineyards subject to a complex system of classification, designed to allow authorization for Port production to be distributed on the basis of potential quality. The system allocates points to a property depending on such factors as grape varieties, viticultural practices, slope, soil type, locality, altitude, aspect and productivity, which are then used to classify the vineyard by a letter from A to F. The higher graded vineyards (*i.e.* A and B) are authorized to turn a greater proportion of their fruit into Port than the lower grades (letters E and F) and the letter attributed to the property influences the price paid for the grapes. For a detailed description of the classification system see Fonseca *et al.* (1987). Generally, the higher ranking vineyards are situated at the lower altitudes in the *Cima Corgo* and *Douro Superior*, where, although the vines are less productive the grapes are considered to be more suitable for premium styles of Port. The *Baixo Corgo* is more productive and produces lighter styles of wines. The total annual authorization is normally of the order of 55 million hl of must, although the total production of the area is usually more than double this volume.

Vines are planted in horizontal rows, either on handbuilt stone terraces, bulldozed earth terraces, or, where the slope permits, in unterraced plots. Recently, some producers have planted on unterraced slopes in vertically aligned rows. All these systems are discussed in Almeida *et al.* (1982) and Felix and Guerra (1999). The type and blend of grape varieties planted are of crucial importance to the quality of the wine (Bakker *et al.*, 1986); effectively most vines consist of an approved Port variety of *Vitis vinifera* field grafted on to a hybrid rootstock, the most common rootstock varieties being Richter 99, Richter 110, 140 Ruggeri, 1103 Paulsen and *Rupestris du Lot* (see Haride and Cirami, 1988). The most desirable red Port varieties are capable of producing tannic, intensely colored wines with pronounced fruit flavors.

In older vineyards, different varieties are usually mixed in the same plot; in the last 15 years increasing knowledge of the qualitative attributes of the traditional varieties has led to a more systematic selection of cultivars and grafting of these separately in large blocks. To some extent this practice mirrors the position in the Douro area towards the end of the 19th Century, when prior to devastation of the vineyards by *Phylloxera*, plots tended to have very high proportions of a particular variety (J.H. Smithes, personal communication). At the time of writing, the regulations governing Port production are being reformulated; however the approved grape varieties are shown in Table 8–4, which must be used in new plantations. As well as these, 36 red and 24 white varieties are tolerated in existing vineyards. Over the last decade a state supported project for further improvement of five of these red cultivars by massal and clonal selection has been in progress. (Magalhães, 1987).

Pruning and training systems are generally *Guyot* (single or double), in older vineyards, or bilateral cordon (see, for example, Freeman *et*

Table 8–4 Recommended grape varieties for production of port[a]

Red varieties	*White varieties*
Bastardo	Códega
Mourisco Tinto	Esgana Cão
Tinta Amarela	Folgosão
Tinta Barroca	Gouveio (Verdelho)
Tinta Francisca	Malvasia Fina
Tinta Roriz	Rabigato
Tinto Cão	Viosinho
Touriga Franca	
Touriga Nacional	

[a]Portaria no. 195/85 of the Portuguese Republic (1985).

al., 1992) in more recently planted sites. In either case the number of buds is restricted to a maximum of 12 per vine. Bilateral cordon is considered to give an effective balance between quality and mechanization of operations such as pesticide spraying and hoeing (Gomes, 1986). Irrigation of vines is not authorized at the time of writing.

Harvesting of grapes normally starts between the end of August and early October, depending on the location of a vineyard and the weather conditions of the season. In the weeks before the vintage, most winemakers will make regular samplings of grapes to determine maturity, usually by simple conventional determinations of dissolved solids, pH and titratable acidity, although juice flavor assessment is gaining some ground as a method to estimate optimum grape maturity (A. Birks, unpublished information; Peres, 1986). Although dissolved solids (which are composed mainly of sugars) in musts destined for Port must legally be above 11 % vol. potential alcohol (Decreto-Lei no. 166/86 of the Portuguese Republic, 1986), in the *Cima Corgo* and *Douro Superior* at least, levels at harvest are often between 12 and 14 % vol. or even higher. Raisining of fruit is generally viewed as detrimental to wine quality. Winemakers will consider that attainment of these values is coincident with the development of optimum levels of fruit flavors and precursors, polyphenolic material (including pigments) and other compounds of importance to quality. The acid composition of grapes harvested at high dissolved solid levels is often low compared with fruit for light wine: total titratable acidity (principally tartaric and malic acids) may be as low as 6 g l^{-1}, expressed as tartaric acid, and juice pH may be up to or even above 4.0 (Peres, 1986; Almeida, 1989).

Vintage

Picking is carried out entirely by hand. Only in some vineyards in the *Douro Superior* would the nature of the terrain permit mechanical harvesting, and at least one grower has carried out machine trials in the area. Grape bunches are cut into plastic or wickerwork baskets or boxes, and transferred to steel bins, commonly of 1 m^3 capacity, for transport to the winery. Wooden open-top barrels, once common for grape transport, are falling into disuse for mechanical and hygienic reasons. Prior to weighing and crushing at the winery a core sample is taken of each bin, and specific gravity in the juice determined, normally by refractometer. The specific gravity may be used to pay a bonus over the basic grape price to the grower.

Vinification

Grapes are transferred from transport bins into large hoppers, whence they are pumped by screw-conveyer to a mechanical crusher. Conventional roller or beater ('centrifugal') crushers are used, and most wineries now remove at least a proportion of stalks from both red and white grapes. Although stalks were included in vinifications in the past (probably because equipment allowing their removal was not generally available), in modern fermentation tanks their inclusion is considered to add undesirable harsh and bitter characters to the wine. As the crushed grapes are pumped to the reception or fermentation tank, sulfur dioxide is added, either as potassium metabisulfite solution or as a solution of SO_2 gas, at levels of between 50 and 150 mg SO_2 per kg of grapes. Many winemakers will adjust

the pH of the must at this stage to around 3.6, using tartaric acid additions.

Since red wines constitute nearly 90 % of Port shipments (Anonymous, 1993), we will consider their vinification first. Fermentation tanks may be inocculated with a selected wine strain of active dried yeast, although most producers still rely on SO_2 additions to select desirable fermenting strains from the natural flora of the grape and winery equipment. Although most modern wineries in the area have fermentation cooling facilities, fermentation temperatures are often maintained around 26 °–28 °C, probably with some effects on the microbial ecology (Fleet and Heard, 1993). The necessity to fortify during the fermentation of grape must means that skin contact time is relatively short: residence time in fermentation tanks is typically about 48 hours. During this time intense maceration is required to extract pigments (anthocyanins) and other phenolic and flavor compounds localized in the grape skins or adjacent cells, and also to prevent the cap of skins and other solids, which rises to the surface with evolution of carbon dioxide, from drying out and developing acetic off-flavors.

Traditionally fermentation was carried out in shallow (1 m) granite troughs (*lagares*), holding 7-5 tonnes of must, and macerated by regular treading sessions of barelegged workers. This practice persists in some wineries and farm premises, sometimes supplemented or substituted by simple pumping systems, and in recent years work has been carried out to reduce the cost in labor and improve the control of this type of vinification. Cooling systems, either by internal coils or panels, or using external heat exchangers, are now common, and in some wineries robotic or piston systems of mechanized treading have been installed. Alternative maceration systems involve remove of fermenting must and recirculating via peristaltic pumping mechanisms. Epoxy-lined stone *lagares* or even stainless steel versions have been built to improve hygiene (Mayson, 1999). In spite of these important developments, most wine is now made in steel fermentation tanks of various forms. Autovinifiers of Algerian conception (Fletcher, 1978; Warre, 1992), which use evolution of CO_2 from fermentation to pump juice to the top of the tank and subsequently spray the cap, are widespread. Disadvantages are that separate systems are required for prefermentative maceration and oxygenation of juice, and in the older cement tanks, arranging adequate cooling is not easy. In some installations autovinifiers have been modified to accept a mechanical helical device known as a *remontadore*, fitted into the top of the tank. Juice is sucked up and sprayed over the cap, the whole operation being programmable. Regular comparisons using grapes of one variety have shown consistently more satisfactory results over autovinifiers in terms of phenolic extraction and aroma (J.K. Burnett, personal communication).

One producer uses thermovinification, in which must is heated at 70 °–75 °C for an average time of 15 minutes before pressing and inocculating with selected yeast. Extraction is thus completed before fermentation, which can take place in any suitable vessel with adequate cooling. Despite its potential for producing dark, fruity wines (Marques Gomes *et al.*, 1977/1979; H.P.R., unpublished results), the process has not found favor with other winemakers. A few wineries have installed rotary closed tank fermenters, and others use pneumatic plunger arrangements, but probably the most common system in the more modern plants is to use mechanical means to remove juice from the bottom of the tank and pump over the top of the must with various forms of fixed spray head. Fermentation cooling can be either via chilled water circulating in jackets round the tanks, external water curtains, or circulation of juice through external heat exchangers. Although fewer wineries have the facilities, must heating is desirable in some years. As well as the effects of fermentation temperature on yeast growth, metabolism and production of flavor compounds, and ecology of the fermentation (Fleet and Heard, 1993), the rate and type of extraction of phenolic compounds from grape solids is influenced. Musts fermented at temperatures above 28 °C show a greater extraction of anthocyanins, giving darker

and preferred young wines, compared with wines made at 22 °C, although these differences and preferences may not be maintained during subsequent maturation of the wines (Bakker, 1989). Pectolytic enzymes offer a further means to increase pigment and flavor extraction, with significant improvements maintained during aging (Bakker *et al.*, 1999), although their use is currently probably not widespread.

Although as described above, some wineries continue to advocate *lagares* and treading to vinify some of their best fruit (Suckling, 1990; Mayson, 1999), there have been few published reports of effective comparisons between different vinification methods and the results are somewhat contradictory. Birks and Sarmento (1991) compared traditional *lagar* vinifications with static pumping over systems, and found the former to give greater extraction of phenolic compounds, and resultant young wines that were considered to be better structured for aging as vintage Port styles (*q.v.*). However, in a similar study, little difference was found during fermentation between *lagar* and tank, and although initially the *lagar* made wine was darker, after two years of barrel maturation significant differences in color and flavor had disappeared (Bakker *et al.*, 1996). Tank design and maceration regimes may well be influential, and it seems likely that individual winemakers will continue to use the system which they feel to be most advantageous.

Whichever vinification system is used, at a predetermined point, depending on the style of wine intended and the original dissolved solids content of the must, the fermenting juice is fortified with wine spirit. The fermentation is typically monitored by measuring the specific gravity of the juice, and when approximately 4–5 % vol. alcohol has been produced, the fermenting liquid in drawn off the solids and mixed immediately with spirit in a wooden, cement or steel vessel. The wet mass of grape solids (pomace) is pressed, using either a continuous screw press, or preferentially, a horizontal piston or pneumatic press. Continuous presses, although still widely employed, can produce bitter and particularly astringent press juice. A proportion of the press juice is normally mixed with the free-run liquid from the tank, the more tannic fractions often being allowed to ferment to dryness separately for distillation material. Blending of wine spirit is generally carried out by pumping a measured quantity of spirit into the reception tank simultaneously with the juice and pressings; vigorous mixing, often with aeration, is then given by circulating the raw wine with an external pump. Some wineries are equipped with dosing pumps or mechanical blending devices for spirit mixing. Wine spirit makes up approximately 20 % by volume of the raw wine. After analysis, alcoholic strength is adjusted if necessary to 18–20 % vol., and pH typically to below 3.6, using further spirit and tartaric acid additions (initial fortification normally causes a significant rise in pH over that of the fermenting must).

White wines are made by similar processes, although there is now a tendency to make lighter styles, particularly of dry white Ports. Maceration on the skins, with concomitant extraction of phenolic compounds giving hard characters to the wine and subsequent browning potential, (Singleton and Esau, 1969) is often reduced to the period up to the visible initiation of fermentation. The juice is then run off and allowed to ferment to the desired point for fortification. Fermentation temperatures are typically lower than in red vinifications, and fractions of the pressings may be mixed with the juice depending on style required and the type of press available. This practice is known as *meia curtimenta*. In some cases, very light wines may be made with little or no skin contact, solids being separated from the free run juice by settling for about 24 hours (sometimes with the addition of pectolytic enzymes to reduce juice viscosity), and fermented after inoculation at low (18 °–20 °C) temperature, to increase formation and retention of fruity and associated aromas. Recent work on the somewhat neglected area of white Port indicates that potential strategies for reducing browning and producing flavor effects via monoterpene alcohols can be developed by the rational use of skin contact and oxygenation (Ho, *et al.*, 1999c). A certain amount of wine is made from *Moscatel* grapes, incorporat-

ing their strongly aromatic characteristics by intense maceration of must, sometimes with partial fortification prior to pressing, to increase flavor extraction. The technique of maceration of skins with alcohol is widely used in the preparation of *Moscatel de Setúbal* in the south of Portugal (Soares Franco and Singleton, 1984).

Basic Styles of Wine

The origin and quality of the must and the shipper's requirements and house style will influence the styles of wine made at the vintage. The majority of wines, red and white, will have between 80 and 120 g l^{-1} residual sugar, having been fortified after consumption of approximately half the original must sugar. Where a shipper requires sweet wines for blending purposes, musts are fortified at the first visible signs of fermentation to produce *geropigas*, containing some 150 g l^{-1} sugar. Red *geropigas*, because of the limited skin contact in their vinification, are lighter and less pigmented than wines of standard sweetness. Some red musts will be allowed to ferment further before fortification, to produce 'dry' (20–50 g l^{-1} residual sugar) wines, also for blending purposes. White *geropigas* are also made, either for blending or for a very sweet style popular in Portugal, and dry white Ports, containing less than about 50 g l^{-1} sugar for aperitif beverages. Red wines will be destined eventually for three basic styles: ruby, tawny or vintage Port. Rubies are wines of between 3 and 5 years average age, matured in wooden vessels but maintaining fruity aromas, firm tannins and appropriately ruby hues. Tawnies are aged longer in wood (up to and beyond 30 years average age), developing amber colors and complex flavors with some oak influence. Vintage Ports are wines from selected vineyards of one year's harvest, of outstanding perceived quality, which are aged in wood for between 2 and 3 years before completion of their maturation in bottle. After at least 10 years further aging they develop characteristic flavors while still remaining full-bodied and fruity. The techniques used to produce these basic styles will be discussed in the next sections. Since white Ports are handled in the cellar in similar ways to red wines (or in the case of some of the more recent lighter styles mentioned above, using techniques akin to those of white table wine production) we will not consider them further.

Aging and Maturation

Young red Port is normally a deep purple-red in color, astringent and harsh from the grape-derived tannins and the spirit congeners. As in red table wines, the color is due principally to anthocyanins, water-soluble pigments originating from the grapes, and in the case of the red varieties listed in Table 8–4, located in the berry skins. The most common anthocyanin quantitatively in Port grapes is malvidin, as malvidin 3-glucoside, followed by malvidin 3-*p*-coumaryl-glucoside and malvidin 3-acetylglucoside, the actual composition varying significantly amongst the cultivars (Bakker and Timberlake, 1985*a,b*). Young wines are normally left undisturbed for two to three months after the vintage, to allow yeast cells, grape solids and precipitated tartrates to settle out, and during this period the visible color of most wines increases to a maximum, a phenomenon often termed "closing up". The effect is believed to be due to the formation of aldehyde- (principally acetaldhyde-) bridged polymers between anthocyanins and other phenolics. This type of reaction probably predominates over direct condensation of anthocyanins with phenolics because of the high levels of free aldehyde (50–100 mg l^{-1}) in young Port compared with red table wines (Bakker and Timberlake, 1986). Aldehydes are both derived from fortification spirit and produced by yeast during fermentation. Arrest of fermentation during its most active phase may maximize levels of acetaldehyde, which otherwise would be reduced to ethanol later (Henschke and Jiranek, 1993), and aeration at spirit mixing (see the section "Vinification") probably contributes to release of free aldehyde by oxidation of bound SO_2 and by promoting coupled oxidation of ethanol.

At the typical pH of finished wine, the aldehyde-bridged oligomers are more colored than the

monomers from which they are derived, and less susceptible to bleaching by SO_2 and the peak color of the wine probably represents an equilibrium between the formation of new oligomers and less colored polymers. As the latter reach a certain size, they become insoluble and precipitate.

These reactions are manifested after "closing up" by a progressive lightening of color, and a change in hue to more ruby tones, followed by gradual browning. The acetaldehyde-anthocyanin condensation products are of a bluish hue, but a new class of brick-red pigments of defined structure which also form during port wine aging has recently been identified. These are typified by Vitisin A which results from reaction between malvidin-3-glucoside and pyruvate (Bakker and Timberlake 1997, Romero and Bakker 1999). It is possible that these pigments are responsible in part for the transition to a redder hue.

After many years in wood storage the wine assumes a characteristic tawny color, these color changes are mirrored by a softening of the astringent and fiery characters, and eventual acquisition of more complex nutty and similar flavors associated with wood extraction (Bakker, 1992). Recent studies demonstrated increases in phenolic compounds in aged tawny ports attributable to wood extraction, which almost certainly contribute to the aged flavor (Ho *et al.*, 1999b).

Most shippers still maintain maturation and finishing facilities ("lodges") in Vila Nova de Gaia, where the wines are normally moved in the first year following their vintage. Wines stored for longer periods in the Douro area, particularly in older uninsulated buildings, may acquire a baked character due to the higher storage temperatures. Both in the lodges in the Douro and in Gaia wines are stored in mature oak vessels, ranging in capacity from slightly less than 600 l ("pipes") to as much as 200 000 l. Pipes or casks are stacked normally four high. Racking regimes vary, but typically range from around 3 monthly intervals in the first year to an annual racking after 3 years. Even in older wines the continuous precipitation of solids necessitates this decanting and subsequent cleaning of the vessels. Cask stacks are emptied progressively from the top row, leaving the lees in the bottom of each cask, which is then removed from the stack and sanitized after removal of the lees. The stack is then rebuilt and refilled row by row. This labor-intensive operation has now been mechanized in some lodges, allowing emptying, cleaning and refilling without disturbing the cask stacks. The choice of vessel size, and thus headspace volume, and aeration at racking, gives the winemaker the opportunity to influence the rate and probably the type of polymerization reactions described above. Generally, wine components destined for ruby and vintage Ports will have a greater part of their aging in large vessels, whereas wines intended for tawnies will be stored predominantly in casks.

Published data on the complexity of other reactions which affect the flavor changes during maturation remains scarce, although well over 100 different volatile compounds have been identified in mature wines (Simpson, 1980; A.A. Williams *et al.*, 1983). Acetate and acetate esters appear to increase with time (older wines have measurably higher levels of volatile acidity, not associated with microbial action) and esterification and formation of, for example, ethyl lactate, diethyl malate, triethyl lactate and monoethyl and diethyl succinate may be indicators of the age of a wine (Ramos and Gomes, 1977/1979; Simpson, 1980; Ramalho, 1991; de Revel et al., 1994). Succinate levels in older wines may also be increased through wood extraction, with possibly some influence on flavor (A.A. Williams *et al.*, 1983). While the concentration of 5-hydroxymethylfurfural, formed through degradation of fructose in acid conditions, can be indicative of wine age (M.A. Williams *et al.*, 1983), its contribution to flavor is probably slight. Other furan derivatives may affect the baked caramelized flavors of older wines (Williams *et al.*, 1986); furans and phenolic compounds have been used, via neural network techniques, to estimate the average age of complex tawny port blends, but their flavor effects are again unclear (Ho *et al.*, 1999a). Conversely, sotolon (3-hydroxy-4,5-

dimethyl-2(5H)-furanone) has recently been demonstrated to be present at higher concentrations in older Ports, and to be linked to the characteristic spicey and nutty aromas of old tawnies, although the mechanism of its formation has still to be elucidated (Ferreira and Bertrand, 1999). Guedes de Pinho *et al.* (2001) examined carotinoid profiles in grapes, musts and port wines from 5 Douro red vine varieties, and concluded that carotinoids identified in wines could be converted to nor-isoprenoids during aging, and affect flavor.

There is little published information on the aging of vintage Port and other bottle-matured wines. Presumably the less oxidative conditions after bottling contribute to lower levels of free aldehyde, and possibly a greater role for the non-aldehyde polymerization route. The abundant deposit which forms demonstrates the effects of polymerization and precipitation. Even after many years in bottle vintage Port retains ruby hues and developed fruit flavors, and not surprisingly differs considerably in character from an equivalent wine aged for the same period in wood. The special case of vintage Port, and the effects of the short initial period in wood (a practice not often imitated by non-European winemakers), remain to be investigated further.

Blending

Blending is fundamental to the quality and style of Port (Goswell and Kunkee, 1977; Ramalho, 1991; Birks, 1992). With the exception of vintage, late bottled vintage and *colheita* Ports (*q.v.*), a shipper will expect to produce products of consistent style and average age. Particularly with younger styles (rubies), where the influence of the base fruit, and hence vineyard and harvest variation, is still strong, the blender is presented with a formidable challenge; the variability of the wines (and the necessity for frequent racking) dictates that the fractional blending system of the *solera* cannot be employed.

Most shippers rely on a series of *lotes*, which are blends of untreated wines ready to feed final shipping parcels, which will be appropriately clarified and stabilized. The *lote*, although normally constituted some months before its expected use in shipment (allowing time for flavors to "marry" and also certain chemical equilibria to be reached), should have acquired the necessary average age and style consonant with the brands for which it is destined. A proportion of the previous *lote* is always included to assist consistency, and sweetness may be adjusted with *geropigas* and dry wines. Sometimes both these may be included in a blend; this apparently illogical process is considered to improve complexity. The backbone of a *lote* is composed of its respective reserves, which are themselves blends of different years, again with the inclusion of a proportion of the previous reserve. The reserves, however, may well differ considerably in style from the final brand, and a blender may maintain, for example, a young dark reserve to give fruit and body to the *lote*, a lighter older version to add complexity and possibly some wood character, perhaps a third reserve of different character, and use these in varying proportions, with *geropigas* and dry wines and even unblended wines if it is felt necessary.

The precise timing of initial blending of young wines to feed the reserves varies from shipper to shipper, but most will begin to combine parcels of similar character within six months of the vintage. Later in the year blends of differing but complementary wines will begin to be formed with a shipping brand in mind. These will eventually form the basis of the reserves, using similar batches from other years, although in the case of old tawnies they may remain for several years before further blending. The conscientious shipper, however, will make regular tastings of all wines in stock, and "refresh" with younger wine if necessary. All these movements, where they involve wines stored in casks, have the same labor implications as described in the section "Aging and Maturation".

Although instrumentation may be used to assist the taster, for example, in maintaining consistency of color (Williams *et al.*, 1986; Bakker and Arnold, 1993), knowledge of the important flavor compounds in Port is still scanty, and we

believe that chemical analysis will continue to play no more than a secondary role in the blending process for the conceivable future.

Commercial Styles of Port

The commercial styles of Port are currently defined by law (Decreto-Lei no. 166/86 of the Portuguese Republic, 1986). At the time of writing, these regulations are being revised. All wines are subject to the controls of the *Instituto do Vinho do Porto*, involving rigorous inspection, analysis and organoleptic evaluation. The rules for the Special Category wines (Anonymous, 1983) are particularly strict, including the maintenance of a current account for a particular *lote*, and are discussed in detail in Fonseca *et al.* (1987).

Wood Aged Styles

Wood aged red Ports can be either rubies or tawnies, this broad categorization being dependent principally on the length of their aging. Ruby wines may be described merely as such, or where their quality is considered exceptional as "vintage character" or sold under a prestigious brand name. Wine of high quality from one year only may be sold dated, as late bottled vintage, which must be bottled between 4 and 6 years after its harvest.

Late bottled vintage is often stabilized and intended for consumption without further maturation, although some shippers produce this style with the intention of completing its aging in bottle. Tawnies similarly may be undifferentiated, or when their quality and average age are considered sufficient may be termed 10, 20, 30 or over 40 years old. This designation refers always to weighted average age of the blend at bottling, and the wines must be approved as such by the *Instituto do Vinho do Porto*. *Colheita* Ports are tawnies from one designated harvest, bottled after 7 years in wood. Late bottled vintage, tawnies with an age designation (10 years old *etc.*) and *colheitas* are all Special Category wines.

White wines are normally sold as described in the section "Basic Styles of Wine", although where their specific gravity is below 1.008 they may be shipped with an alcoholic strength as low as 16.5 % vol., being termed light dry white Port.

Bottle Aged Styles

As described in the section "Basic Styles of Wine", vintage Port is a wine or blend from one outstanding year, bottled between 2 and 3 years of the harvest, and is subject to the Special Category rules. Usually a vintage will bear the name simply of the shipping house, although there is a growing tendency to produce wines from one property, or "single *quinta*" vintages. The declaration of a vintage, an event of some notoriety, takes place between January and September of the second year following the harvest, following approval by the *Instituto do Vinho do Porto* of a specific *lote*. Although the selection of the outstanding year is the criterion of the shipper, and may be dependent to some extent on the particular areas in the demarcated region where his grape supply is concentrated, there is usually a reasonable degree of consensus amongst major shippers, who will declare a vintage on average every three or four years.

Crusted Port is normally a blend of wines of different years, bottled after rather more aging in wood than vintage Port, but with the intention of completing its maturation in bottle. As its name suggests, and like vintage Port, it throws an abundant precipitate in bottle. Some of the characteristics of mature vintage Port are developed, but without the capacity for long aging of the latter style.

Processing

Processing of Port after aging generally follows conventional oenological practices. Clarification normally involves fining with proteinaceous agents such as gelatine, egg white or casein. Bentonite may be used for white wines to remove unstable protein fractions. Some producers use centrifugation, which may be employed with young wines to reduce deposition during aging. Most rubies and younger tawnies are cold stabilized to remove unstable tartrates, coloring

matter and colloidal material. The two systems most commonly used are passage through a heat exchanger and ultracooler to reduce the temperature to about −8 °C, followed by a static holding period of about one week in insulated or cooled tanks, or continuous systems, which chill the wine and pass it continuously through a crystallizing tank, where potassium bitartrate crystals are concentrated in suspension and provoke nucleation and further crystallization (Simões, 1977/79). In either case, cold wine after the stabilization process is filtered using diatomaceous earth followed by sheets and perhaps cartridge membrane or depth filters. Crossflow microfiltration (Gibson, 1988) has been used at pilot level, either pre- or post-cold stabilization, but is as yet not employed on an industrial scale. Flash pasteurization subsequent to cold treatment has been recommended to inhibit further precipitation of macromolecules (Azevedo, 1963/64), and some shippers still apply the process to younger wines, although possibly increasing the concentration of ethyl carbamate (Barros and Bertrand, 1990; see the section "Ethyl Carbamate"). Recently trials have been carried out using electrodialysis (Goncalves et al., 1999) for stabilization of Port, with apparently favorable results compared with classical systems in terms of flavor, energy and filtration costs.

Bottling or bulk shipment may be preceded by membrane filtration using pore sizes of 1.2–3.0 u. Stopper corks are normally used for all styles except vintage, crusted and some late bottled vintage Ports; for these wines driven corks are employed given that their aging should continue in bottle. Bottle matured styles are not cold stabilized and rarely filtered; the formation of heavy deposit and the necessity for decanting are considered essential to the final product.

MADEIRA

Regulation and Geographical Origin

Madeira is the fortified wine made on the islands forming the autonomous administrative region of Madeira, in the Atlantic Ocean. Although the demarcated area includes all the islands forming the archipelago (Decreto Regulamentar Regional no. 20/85/M. Região Autónoma da Madeira, 1985), effectively all Madeira is now produced from grapes grown on the main island ("Madeira"), the limited production on the other inhabited island of the group, Porto Santo, being vinified and sold locally as table wine. The major plantations for Madeira grapes are on the south coast, east and particularly west of the capital Funchal, and on the north coast. Plantation in the north has expanded in the last 15 years, to some extent provoked by encroachment by building and banana plantations in the traditional areas on the south of the island. The vineyards are generally on steep slopes of volcanic soil, and may vary in altitude from sea level to 700 m, with obvious climatic differences. The climate is damp and frequently misty, and vineyard aspect is thus of paramount importance in maximizing incident sunlight. Annual rainfall is of the order of 750 mm, falling mainly in the period October to April, and daytime temperatures in the lower areas range from 16 °C in winter to 27 °C in summer.

The *Instituto do Vinho da Madeira* is responsible for the control of Madeira in much the same way as the *Instituto do Vinho do Porto*. Vineyard plantation must follow the recommendations of the regional agricultural services.

Viticulture

Vineyards on Madeira are typically small (the largest mature vineyard at the time of writing is about 3.5 ha, although cultivation of larger areas is under way), densely planted (7 000–8 000 vines per ha), and labor intensive, being trained on low trellises or wires, and often on small walled horizontal terraces. Mechanization of traditional vineyards is almost non-existent. Pruning systems are generally based on single *Guyot*, and frequently a secondary crop is grown beneath the trellises. Water from the higher areas of the island is often channeled to lower levels in open ducts known as *levadas*, although irrigation of vines is only contemplated in adverse conditions and with special governmental authorization.

Recommended grape varieties for Madeira production are those shown in Table 8–5; of these, the white varieties are considered to be the "classic" cultivars, having given their names in the past to styles of Madeira, and the red *Tinta Negra Mole* is currently the most prolific. At the beginning of the 20th century, as much as 80 % of the fruit produced in Madeira was from direct-producing (*i.e.* ungrafted) hybrids between *Vitis vinifera* and American vines, and although wine made from this fruit was incorporated into Madeira blends (Cossart, 1984), its use is forbidden under EU regulations. Efforts have been made in recent years to increase the proportion of *Vitis vinifera* plants, particularly the classic white varieties mentioned above. The regional agricultural services are active in supplying pregrafted vines of the "noble" varieties to farmers, and at least one shipper has planted substantial dedicated vineyards with training systems designed to maximize the relatively low sunshine hours. The immediate future viticulturally in Madeira is therefore promising in heralding a return to larger production of the traditional varieties.

Vintage

The earliest date for harvest is fixed annually by the *Instituto do Vinho da Madeira*, and is normally towards the end of August. Grapes must have at least 9 % vol. natural potential alcohol for Madeira. Picking, at one time into conical baskets, is now predominantly into plastic boxes and wooden or steel transport bins. The colorful practice of transporting must to a fermentation site in goat skins (Cossart, 1984) is no longer used.

Table 8–5 Recommended grape varieties for production of Madeira[a]

Red varieties	*White varieties*
Bastardo	Sercial
Tinto da Madeira	Boal
Malvasia Roxa	Malvasia Cândida
Verdelho Tinto	Terrantez
Tinta Negra Mole	Verdelho Branco

[a]Decreto Regulamentar Regional No. 20/85/M (1985).

Vinification

The traditional winemaking methods described by Cossart (1984) and Goswell and Kunkee (1977) have all but died out, and major producers now rely increasingly on standard vinification techniques. White grapes are crushed with sulfur dioxide additions, and either separated from the skins and pulp before fermentation, when press juice may be fermented separately or mixed with the free run fraction, or given some maceration before pressing (analogous to the *meia curtimenta* described in section 5.4). Continuous screw presses are giving way to batch presses, either pneumatic tank presses or the hydraulic piston variety. The use of selected yeast inoculation is not customary. Red fruit is normally macerated during fermentation, using either autovinifiers as used in Port production, or by conventional pumping over systems (*remontagem*). Where initial sugar contents are low, chaptalization with concentrated grape must is usual prior to fermentation. Acidity adjustment normally is not necessary, the grapes having naturally a relative low pH (less than 3.5) and high titratable acidity at harvest.

Fermentation cooling is desirable in the tanks now in use, a temperature of 26 °C being considered a suitable maximum, and fermentation progress is followed by specific gravity measurement. Whereas until relatively recently most wines were fermented dry, to be fortified during the months following the end of fermentation, and sweetened with various preparations at a later date, the tendency amongst shippers now is to follow the Port system of fortifying to about 17.5 % vol. during fermentation, leaving appropriate levels of residual sugar (partially from the Madeira grapes, partially from chaptalization) for the various basic styles of wine. Thus malolactic fermentation, once common in Madeira wine, is eliminated, and concomitant increases in volatile acidity avoided. The point of fortification depends on the desired sweetness of the final wine; *surdo*, a sweetening wine, is made by fortification before the onset of fermentation, and is analogous to Spanish *mistella* and the *geropiga* of the Port area.

Aging and Maturation

Most Madeira undergoes some form of heating process during maturation, to accelerate the aging process. The majority of wines are heated in special vessels known as *estufas*, which are closed tanks made of wood, cement or, more recently, stainless steel. Heating is by circulating hot water, either through a stainless steel heating coil in the tank, or in the modern steel *estufas*, by a hot water jacket. In the latter trials are currently in progress with mechanical agitation to give more even heating. Heating tanks must be sealed by the *Instituto do Vinho da Madeira*, and the process must by law be prolonged for at least 3 months at a maximum temperature of 50 °C. In practice, most shippers prefer 45 °–50 °C. As well as wines of sweetness levels corresponding to the finished styles, some *surdos* may be given this treatment. The flavor changes in this process are dramatic, and the wine acquires an aged brown hue, caramelized aromas, and softer palate through effects on the polyphenolic material. Somewhat surprisingly, there are few references in the literature to the chemical changes occurring during this interesting process. There is an increase in levels of ethyl carbamate (Ferreira and Fernandes, 1992; see also the section "Ethyl Carbamate") and presumably a substantial rise in HMF concentration, amongst other changes.

Other wines, particularly those limited quantities made exclusively from the "noble" white varieties may be subjected to more gentle heating for longer periods, in systems known as *canteiro*. In its simplest form, the system involves keeping wine in casks in a suitably warm part of the aging premises, for example near the roof on an upper storey. Where desirable, the casks can be stacked in the area of the *estufas*, preferably at a higher level, where in spite of the insulation on the heating vessels, the ambient temperature can be significantly above that of the rest of the cellar. These treatments are considered to be more beneficial to the varietal flavors of these white wines than *estufagem*. The practice of heating warehouses by steam pipes for accelerated aging in casks (Goswell and Kunkee, 1977) seems to have died out.

Madeira wines are predominantly wood aged, apart from their period in the *estufa*. Vintage Madeira, made only from the "noble" varieties, is wine from one year only, which must be aged for a minimum of 20 years in wood and two in bottle. Bottles are stored upright, and it is customary to re-bottle at periodic intervals, disgorging and aerating the wine. This labor intensive process ensures an expensive product matured through a possibly unique system.

Blending

Blending of the basic house styles normally follows a simplified version of the system used by Port shippers: wines will be blended at some stage after their *estufagem* into reserves which will feed the *lotes* on which the final shipping wines are based. At the *lote* stage the sweetness will be adjusted with *surdo*, and to a lesser extent with concentrated grape must, sometimes the rectified product. As with the Port system, a proportion of the *lote* will be held back to form the basis of the next blend, assuring the consistency of the final product.

Solera wines are blended using a system with some similarities to that used in Jerez. Wine of recognized high quality is stored in casks, the vintage year of this first parcel being the date attributed to the *solera*. During the first five years the casks can be topped up only to compensate for evaporative losses, using good quality wine. After this period the shipper may begin to bottle the wine, at a rate of 10 % of the total volume per year, topping up with younger wine, but of similarly high quality as the original parcel. This process can continue for a maximum of ten additions, when the whole of the remaining volume of wine must be bottled. The average age of the final blend necessarily adds to the expense of *solera* wines.

Commercial Styles of Madeira

Considerable efforts are being made to increase grafting of the classic white grape varieties, although much Madeira is still made from

Tinta Negra Mole. Hence the varietal descriptors *Sercial, Verdelho, Boal* and *Malvasia* (or Malmsey), are now used only for those wines of predominantly single-variety origin. Shippers have now adopted terminology such as "special dry", "medium dry", "medium rich" and "full rich" to describe the major styles of finished wine. Certain types of wine and terminology are defined by law (Portaria no. 40/82 of the Portuguese Republic, 1982). The expression "dry", "medium dry", "medium sweet" and "sweet" correspond to wines with specific gravities of below 1.011, 1.011–1.019, 1.019—1.026 and above 1.026 respectively. Some styles are sold with an indication of the minimum age of the blend, under the titles "extra reserve", "old reserve", "reserve" and "superior" corresponding to ages of 15, 10, 5 and 3 years respectively. The attractively named "rainwater" is a medium gold colored high quality style, dry or medium dry, and with a minimum age of three years. Details of these styles are given in Cossart (1984).

Processing

The processing of Madeira follows current oenological practice. After *estufagem* many wines will be fined with activated charcoal to remove unpleasant aromas associated with the heating. Standard styles will be fined with casein to lighten color if necessary, bentonite to remove unstable protein fractions, and gelatine for physical clarification. Despite precipitation during aging, many wines are not cold stable, and receive standard refrigeration treatment prior to bottling (−8 °C for about a week), followed by keiselguhr filtration. Prebottling filtration can be by sheets or sheets followed by cartridge. Stopper corks are generally used, except for the aforementioned vintage Madeiras.

QUALITY ASPECTS

Ethyl Carbamate

The origins and levels of the suspected carcinogen ethyl carbamate (urethane) in wine have received considerable attention in recent years (Dominguez and Goswell, 1989), research having been directed fundamentally towards identifying precursors and minimizing their formation (Hensche and Jiranek, 1993). The major mechanism of urethane formation is considered to be urea ethanolysis, urea having been excreted during fermentation as a result of arginine metabolism (Ough *et al.*, 1988*a,b*; Monteiro *et al.*, 1989). The concerns over urethane in fortified wines are twofold: fortification at the approximate midpoint of fermentation, as in much Port and Madeira, occurs at a point when urea concentration in the must has been reported to be at a maximum (Barros and Bertrand, 1990; Daudt *et al.*, 1992), and the heating involved in the *estufagem* process tends to raise the rate of formation of ethyl carbamate from urea. Thus these techniques theoretically maximize potential ethyl carbamate or the compound itself. However, studies on the levels of ethyl carbamate in Ports (Barros and Bertrand, 1990) and Madeiras (Ferreira and Fernandes, 1992) showed that levels in finished wines were in general well within current guidelines, and indeed in the Madeira work indicated that potential ethyl carbamate may be higher in wines allowed to ferment to dryness. This finding is supported by recent work with Port fermentations (Watkins, 1998). In spite of these results, fortified winemakers may be obliged to consider future changes in technique, such as the use of low urea-excreting strains of yeast, and pay particular attention to the content of urethane in fortifying spirit.

Microbial Spoilage

Although many of the bacterial problems encountered in wine in the past have been eliminated by improved hygiene and better understanding of the process, and despite the high alcoholic strength and low pH of most fortified wines, there remain some troublesome strains capable of spoiling the wines described here (Goswell, 1986). In Sherry, particularly in the *flor* process, acetification by heterofermentative lactic acid bacteria can be a problem (Fornachon, 1969), and is normally controlled by judicious

use of sulfur dioxide, membrane filtration and alcohol additions. Great care must be exercised with the latter so as not to terminate the *flor* activity. In wines with residual sugar, such as Port, spoilage by ethanol tolerant heterofermentative *Lactobacillus* species can lead to significant levels of acetic acid production through degradation of hexose sugars. The organisms involved appear to be predominantly strains of *Lact. hilgardii* (Fornachon, 1969; Couto and Hogg, 1994), although other species of *Lactobacillus* have been isolated from spoiled fortified wines. Detection of spoilage typically has been by increase in volatile acidity, although recent work has shown that the conversion of L-malic to L-lactic acid occurs before other detectable spoilage parameters are evident, and thus monitoring of L-lactic acid could be an effective early indicator of bacterial alteration (de Revel *et al.*, 1994). Metabolism of certain amino acids by *L. hilgardii* has also been shown to precede classical indicators of spoilage, as well as resulting in the formation of ethyl carbamate and its precursors (Hogg, *et al.*, 1994; Azevedo and Hogg, 1997).

Strategies for dealing with these problems include rigorous hygiene, beginning in the vineyard, and attention to such factors as alcoholic strength and pH. Pasteurization has been the method of choice for eliminating the microorganisms; membrane filtration through pore sizes sufficiently small to remove bacteria is not easy with sweet red wines. Great difficulties can be experienced in sanitizing wooden vessels which have held spoiled wine, not least in removing the aromas associated with spoilage.

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9

From Vine to Cognac

R. Cantagrel and B. Galy

INTRODUCTION

The quality of Cognac spirits is unanimously recognized throughout the world. This is the result of the determination shown by the wine-growers and traders in conquering a quality market. For the professionals of the region, wine-growers and traders, it was necessary to:

- determine the best growing areas, as the vineyards were extended
- select vine varieties which were better adapted to distillation; hence the appearance of the Ugni blanc variety.
- combat diseases of the vine for a harvest of healthy grapes
- harvest and process in keeping with traditional methods, while integrating inevitable developments in mechanization
- perfect the stills, helped by a fruitful collaboration with local manufacturers, notably in determining the best proportions between the volume of the pot, that of the cap and swan's neck and the length of the condenser coil
- improve distillation techniques by carrying out two successive distillations, and producing a spirit which is smoother and finer, and higher in alcohol
- respond to the desires of a consumer who is more and more exacting
- select and encourage the best spirits
- research with the coopers to find the best oak casks for aging
- combat fraud by respecting the inherent characteristics of products of the area
- increase analytical and organoleptic controls.

THE GEOLOGY AND THE 'CRU' (GROWTH AREA)

The geographical area used for cognac production is split administratively by the decrees of 1 May 1909 and of 15 May 1936. It includes nearly all of Charente Maritime, a very large part of Charente and some neighboring communes of Deux-Sèvres and of the Dordogne. The vine area totals some 82 000 ha. Within this geographic zone were formed subdivisions of designated areas or 'crus' (decree of 13 January 1938), as a function of the particular characteristics of the spirits produced (Audemard *et al.*, 1973):

- Grande Champagne,
- Petite Champagne,
- Borderies,
- Fins Bois,
- Bons Bois,
- Bois Ordinaires.

THE VINE VARIETIES

According to the decree of 11 March 1971, the wines destined for distillation to obtain Cognac spirits must originate from the following wine varieties:

- principal vine varieties: Ugni blanc, Colombard, Folle Blanche,
- auxillary vine varieties are accepted up to a maximum proportion of 10 % of the blend: Semillon, Blanc ramé, Jurançon blanc, Montils, Select.

The Ugni blanc variety today represents more than 95 % of white grape varieties of the region. It is a late vine, vigorous and productive. It gives, in the Cognac region, wines with very high acidity and low alcohol, appropriate for distillation. The spirits are fine, fragrant and a little dry.

The Colombard, a late-ripening vine variety, is a good producer. It is sensitive to oïdium disease and grey rot. The wines are of good quality, fragrant and with an odor of flint. The spirit lacks a little fineness. The Folle Blanche is unfortunately sensitive to black and grey rot. It gives spirits that are rounded and rich, with a greater bouquet, a long-lasting aroma and appropriate for long aging.

The Montils, classified as 'recommended', is a good producer. The spirits are fine and floral. Galy *et al.* (1992a) demonstrated big differences between these vine varieties for three alcohols whose origin is linked to the variety: hexanol, *cis*-3-hexenol, α-terpineol (Table 9–1). These differences exist independently of the year of harvesting, the location and the winemaking or distillation techniques. The Folle Blanche and the variety obtained by crossing it with the Ugni blanc (INRA 8476) are richer in α-terpineol. The Colombard shows the highest levels of hexanol, while the Ugni blanc contains the most *cis*-3-hexenol.

On tasting, the spirits of the different vine varieties also present specific characteristics (Table 9–2):

- the Montils is appreciated for its fineness and the intensity of its aroma
- the Folle Blanche possesses aromas that are less fine, but very rounded which develop well with aging
- the Colombard, is described in terms reflecting the high levels of hexanol ('green' flavor) of the spirits.

Table 9–2 shows the potential of two vine varieties of the Appellation Controlée zone, Montils and Folle Blanche, put aside today in favor of the Ugni blanc.

Table 9–1 Average levels of the three most discriminant compounds in spirits (mg/l of spirits at 70% vol.)

Vine variety	*Hexanol*	*cis-3-Hexenol*	*α-Terpineol*
Montils	17.5	0.59	0.19
Folle Blanche	11.7	1.19	0.41
Ugni blanc	13.4	2.16	0.20
Colombard	39.1	1.46	0.17
Folignan[a]	4.1	0.08	0.65

[a]A variety obtained by crossing Folle Blanche with Ugni blanc which is being tested but is not yet authorized for cognac.

Table 9–2 Organoleptic characteristics of the spirits of different vine varieties

Vine-variety spirits	*Organoleptic descriptors*
Ugni blanc	Flora, spicy, confectionery
Folle Blanche	Rounded, very aromatic after aging, aromas of lime tree and violet
Colombard	Sharpness, heavy and lacking fineness
Montils	Floral, fruity, aroma of tropical fruit and licorice

THE WINEMAKING

The quality of the spirits depends largely on that of the wines. Achieving this quality starts with the vine and continues all year long in efforts to obtain a healthy harvest and optimal maturity. In Table 9–3, we present the significant climatic events for the years 1987 to 1997 which governed the potential for production and, to a great extent, the organoleptic characteristics of the wines and the spirits.

The production of wines destined for Cognac has certain characteristics which distinguish it from table wine production (Figure 9–1). The scientific basis of these characteristics is becoming more and more established.

Table 9–3 Summary of the climatic conditions of the last six years, and the principal characteristics of the harvests

		Alcohol (% vol.)	*Yield (hl/ha)*	*Acidity (g/l H_2SO_4)*
1987	Frost to − 19 °C, rapid bud burst, drop in temperatures during blossoming, sudden end of blossoming (very hot periods at the end of June), high temperatures in September, considerable precipitation in October (200 to 300 mm), rapid deterioration of foliage, big drop in alcohol, rapid development of *Botrytis*	7.5	123	8.69
1988	Winter and springtime rainy, rapid and very aggressive evolution of mildew, exceptional sunshine with hot days until November, good ripening	9.5	84	9.00
1989	Not much rain, a lot of sun throughout the year, which was sun "early"	10.9	111	7.07
1990	Winter was mild, temperatures rather high throughout the year, apart from the irregular temperatures of springtime, not much rainfall, much sunny weather, some symptoms of drought during the summer	9.8	190	6.14
1991	Generalized springtime frost, a cold springtime, very good conditions in summer, considerable catching of ripening	9.64	48	8.56

continued

Table 9–3 *(continued)*

		Alcohol (% vol.)	*Yield (hl/ha)*	*Acidity (g/l H_2SO_4)*
1992	Dry winter and spring, numerous summer storms, localized hail damage, considerable in places, some plant protection problems (mosaic mildew, main-stem rot), exceptionally wet autumn slow ripening	8.01	163	9.05
1993	Very dry winter, very bad bud bust, serious chlorosis damage, variable spring weather conditions, good initial ripening followed by a very wet period, difficult final ripening with rapid development of grey rot.	7.77	91	9.96
1994	Mild, very wet winter. Spring frost affecting 5 to 10 % of the growing area. Rather wet spring. Dry beginning to the summer, then very cold wet weather in September producing high levels of rot. Very good harvest conditions.	8.61	125	8.71
1995	Mild damp winter, late spring frost affecting about 15 % of the vines. Hot weather during flowering and summer drought, then a cold and very wet month of September. Very good weather again during the harvest, with an appreciable concentration effect.	9.74	114	6.82
1996	Cool spring, very rapid flowering during very hot weather, extremely variable summer weather conditions, excellent ripening in good sun and cool temperatures producing, as a result, little rot and high acidity.	9.76	135	7.99
1997	Very early bud burst, several frosts affecting a total of 15 % of the vines. Good flowering but difficult berry setting, very vigorous and prolonged growth compensating for the early start to the year, very good ripening producing no rot but low acidity.	10.38	?	6.94

Treatment of the Grapes in the First 5 Minutes

The principal changes that occur in the first 5 minutes during treatment of the harvest are shown schematically in Figure 9–2 (*Guide of Charente Winemaking*, 1992) The intensity of these changes is a function of the conditions of treatment of the harvested grapes.

From the Harvest to the Fermentation Vat

The harvesting machine was introduced and developed in the early 1970s and became known in our region very rapidly. It is used now by more than 90 % of the vineyards. The grape is subjected to a certain number of mechanical operations, which can have a considerable influence on the quality of the future spirits. Three criteria need to be taken into account:

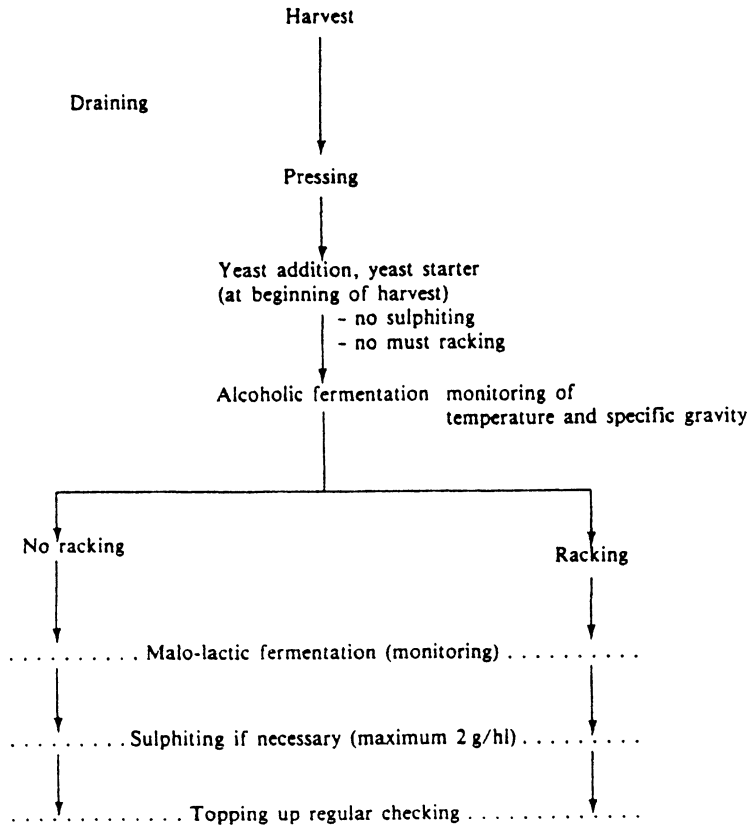


Figure 9–1 The Charente winemaking process.

- The grape needs to be treated with care, crushing which is too forceful may cause the appearance of defects ('green' or 'kerosene-like' characteristics) (Table 9–4).
- The production of solids and their liberation in the must should be limited. Excess solids are undesirable in Charente winemaking because of the risk of increased higher alcohols in the spirits.
- The chain from the initial site of harvesting to processing needs to be rapid, in order to minimize waiting periods or the stocking of the grape crop before pressing (maceration, oxidation, etc.)

Table 9–5 shows the effects of the different treatments of the harvested grape on the composition and quality of the products obtained.

The Fermentation

Once extracted, the juice from the grapes is fermented in the vats in which the wine will stay until distillation. The essential aromatic constituents of the new spirit are formed during fermentation and storage. The Station Viticole seeks to improve knowledge of these stages and to have a better control over them.

The yeasts are naturally present in the grape must and multiply during the winemaking process to reach a population of 10^7 to 10^8 cells/ml must at full fermentation. Park (1974) counted more than 650 yeasts divided into 31 species and 11 genera. Ribes (1986), Park (1974) and Versavaud *et al.* (1992) showed that a fragile natural balance existed between the different species, and that this balance varied between the vine, the

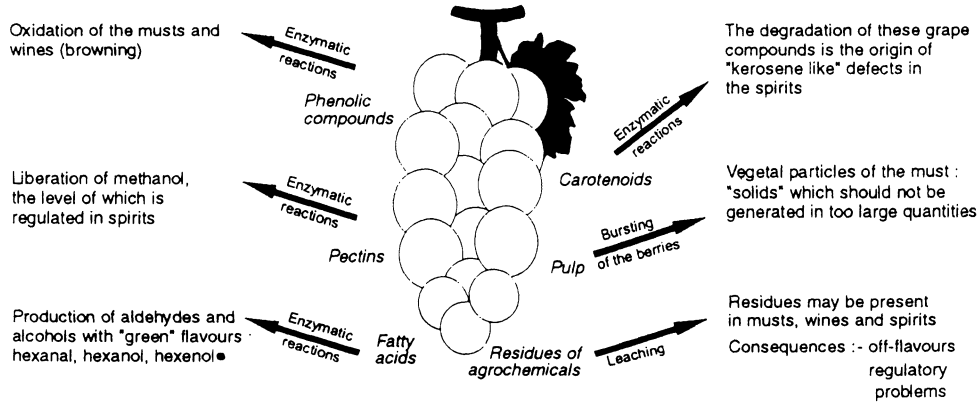


Figure 9–2 Changes that occur in the first 5 minutes of the treatment process.

warehouse and the fermentation vat (where practically only one species is dominant, *Saccharomyces cerevisiae*).

The principal reactions converting the grape sugars (glucose and fructose) to alcohol and carbon dioxide are accompanied by secondary reactions which lead to the formation of several constituents (esters, higher alcohols, glycerol, pyruvic acid, succinic acid, butanediol, etc.). Given that the yeast species possess different potentials to synthesize the aromatic constituents and that the expression of these potentials varies according to the composition of the must (acidity, pH, sugars, etc.) and the fermentation conditions (temperature, oxygen), we can better understand the variability in the composition of the wines. Variation in the yeast flora is one of the aspects of the wider notion of the soil and the growth area in the determination of the final bouquet (Figure 9–3).

Our work has shown that intensive yeasting with commercial active dry yeast (ADY) gives distillates of inferior quality to those obtained with natural yeasts under normal fermentation conditions. Consequently, studies concerning the natural microflora of the region and their importance in the formation of quality, as well as in the control of yeasting operations, have been carried out. The ultimate objective is the selection of a yeast preparation made up of strains of *Saccharomyces cerevisiae* which are the most representative and probably the most adapted to the conditions of Charente winemaking.

Table 9–4 Compounds responsible for defects in the Cognac

Compounds	*Defects*	*Limits in new spirits[a] (mg/l)*
Hexanol	Green	20
cis-3-Hexanol	Green	3.5
TDN (1,1,6-Trimethyl-1,2-dihydronaphthalene)	Kerosene like	1
Higher alcohols	Without constituting a major defect, a value greater than 3500 mg/l for the sum of the higher alcohols (new spirit) arises from certain winemaking problems, the origin of which should be found (e.g., excessive amounts of solids in the must)	

[a]These values are only an indication and are based on statistical results obtained by the Station Viticole.

Table 9–5 Adverse effects on quality observed during the different phases of the grape crop

Factors studied	*Parameters influenced*[a]		*Evolution*[b]	*Organoleptic aspects (spirits)*
Crushing				
Mechanical harvesting and transfer of grapes: crushing, pumping	TDN	(M, W, S)	↑	'Kerosene-like' notes
	Must deposit	(M)	↑	
	Higher alcohols	(W, S)	↑	Loss of fineness
Destemming	Stalks	(G)	↓[c]	
	Gross vegetation debris	(G)	↓[c]	
	Shredded leaves	(G)	↑	
	Leafstalks	(G)	↑	
	pH	(M)	↑	
	TDN	(M, W, S)	↑	
	Hexanol	(M, W, S)	↑	'Green' flavors
	cis-3-Hexen-1-ol	(M, W, S)	↑	
	Must deposit	(M)	↑	
	Laccase units (*Botrytis*)	(M)	↑	'Moldy' flavors
Maceration	Phenolic compounds (OD 280 mm)	(M)	↑	
	Oxidation (OD 420 nm)	(W)	↑	'Green' flavors
	Stability to air	(W)	↓	
	Diffusion of agrochemicals	(M, W, S)	↑	Flavors of agrochemicals (sulphur, earthy, pharmaceutical)
Excessive pressing	pH	(M)	↑	
	Acidity	(M)	↓	
	Potassium	(M)	↑	
	Phenolic compounds (OD 280 nm)	(M)	↑	
	Oxidation (OD 420 nm)	(M)	↑	'Green' notes
	TDN	(M, W, S)	↑	'Kerosene-like' note
Insufficient filtering mass of the pomace	Must deposit	(M)	↑	
	Higher alcohols	(W, S)	↑	Loss of fineness

[a]Parameters influenced analyzed on: grape crop (G); must (M); wine (B); spirit (S).
[b]Evolution: increased (↑); decreased (↓)
[c]Favorable consequences on the quality.

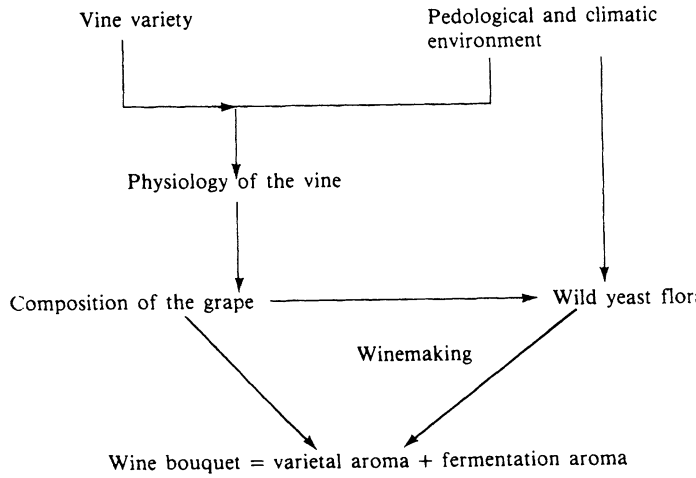


Figure 9–3 The origin of the wine bouquet.

Table 9–6 and 9–7 review the principal factors studied during the course of winemaking, their influence on the wine and spirit composition and their qualitative impact (Galy *et al.*, 1992b). This shows the complexity of the winemaking process and the need for careful checks at each stage.

THE CHARENTE DISTILLATION

The Charente distillation process for the production of Cognac spirits is governed by a number of precise regulations defined by decree.

The total capacity of the still is limited to 30 hl, corresponding to 25 hl of useful load. The heating must be by open fire: gas is the form of energy most used these days.

Two successive distillations are necessary to obtain a spirit with an alcohol strength of no more than 72 % vol. The distillation of the wine produces the *brouillis* of a general alcohol strength of between 27 % and 30 % vol., depending on the initial strength of the wine. The *brouillis* in its turn is submitted to distillation: this is the second distillation or *bonne chauffe* which generates several fractions: the heads, the heart or spirit cut, and the seconds. The rate of passing over of each volatile constituent of the wine or of the *brouillis* depends on its physico-chemical characteristics (Figure 9–4), (Cantagrel *et al.*, 1990).

- The heads contain the most volatile elements which are often detrimental to the quality of the spirit. Their volume represents 1 to 2 % of the volume of the batch.
- The heart contains the most noble constituents of the aroma in their ideal proportions. It constitutes the authentic cognac spirit which will be submitted to maturation.
- The seconds pass over after the spirit cut: these are still rich in alcohols, but contain less-volatile components which need to be recycled, in order not to spoil the fineness of the spirit.

While remaining within the framework defined above, certain differences can exist between the distillation techniques advocated by different trading houses (e.g. proportion of the fine less, recycling of seconds to the wines or the *brouillis*). These particularities allow each house to confer an authentic character to their spirits, corresponding to their customers' expectations.

THE AGING OF COGNAC

The process of maturation of the spirits and its effect on the composition and the quality of

Table 9–6 Enological consequences of different fermentation conditions

Factors studied	*Parameters influenced*[a]	*Evolutions*[b]		*Organoleptic aspects (corresponding spirits)*
Hyperoxygenation	Oxidation of phenolic compounds (OD 420 nm)	(M)	↑	Qualitative amelioration
		(W)	↓	
	Isoamyl and phenylethyl acetates	(S)	↑	Balanced, harmonious rounded full-bodied, floral, but loss of typicity
Must racking	Must deposit (complete elimination)	(M)	↓	
	Yeast nutritive elements	(M)	↓	Loss of character and typicity
	Yeasts	(M)	↓	
	Higher alcohols	(W, S)	↓	
Yeasting				
Yeast starter (natural yeasts) or ADY	Latent period	(M + W)	↓	Fineness, typicity
Commercial ADY				Loss of aroma richness
Fermentation temperatures	Higher alcohols	(W, S)	↓	
Low temperatures (at 18 or 22 °)	Esters of fatty acids	(S)	↑	
	Ethanal	(W, S)	↓	
	Acetals	(W, S)	↓	
	Acetates of higher alcohols	(S)	↑	Very floral and very fruity, loss of typicity only at 18 °C
At 22 °C				Agreeable character: floral, round, rich, confectionery
At higher temperatures	as above	Opposite variations for the same compounds		Loss of fineness, 'green', vegetal notes

[a]Parameters influenced analyzed on: must (M); wine (W); spirit (S).
[b]Evolution: increase (↑); decrease (↓).

Table 9–7 Enological consequences of different conditions of wine storage

Factors studied	*Parameters influenced*[a]		*Evolutions*[b]	*Organoleptic aspects (corresponding spirits)*
Storage of wines				
Decrease of pH	Ethyl lactate	(W)	↑	Qualitative improvement
	Ethyl succinate	(W)	↑	
	Ethyl acetate	(W, S)	↑	
	Oxidation (OD 420 nm)	(W)	↓	
	C_{13} Norisoprenoids	(W)	↑	
Sulphur dioxide (reserved for fragile wines spoiled grapes)	Oxidation (OD 420 nm)	(W)	↓	
	Lactic acid bacteria	(W)	↓	
	Acetic acid bacteria	(W)	↓	
	Ethanal	(W, S)	↑	
	Acetal	(W, S)	↑	
• At 2 g/hl of wine				Increase of fineness and floral character, but risk of increase of ethereal character
• At 4 g/hl of wine				Qualitative alteration
Temperature				
• cooling after MLF	Esters of fatty acids	(S)	Limited hydrolysis	More intense floral character
Duration of storage (0 to 5 months)	Ethyl lactate	(S)	↑	Intense aromatics increase then decrease
	Ethyl succinate	(S)	↑	
	Acetal	(S)	↑	The fineness of aromas decrease
	Norisoprenoids	(S)	↑	
	Ethyl acetate	(S)	↑	
	Ethyl formate	(S)	↑	
	Isoamyl and phenylethyl esters	(S)	↓	
	Ethyl caprylate	(S)	↓	
Malo-lactic fermentation (MLF)	Lactic acid	(W)	↑	
	Ethyl lactate	(W, S)	↑	
	Ethanal	(S)	↓	
	Acetal	(S)	↓	
Before MLF and during MLF				Floral and fruity character
After MLF	Isoamyl and phenyl ethyl ecetates	(S)	↓	Less fruity aromas, rounder and more winey

[a]Parameters influenced analyzed on: must (M); wine (W); spirit (S).
[b]Evolutions: increase (↑); decrease (↓).

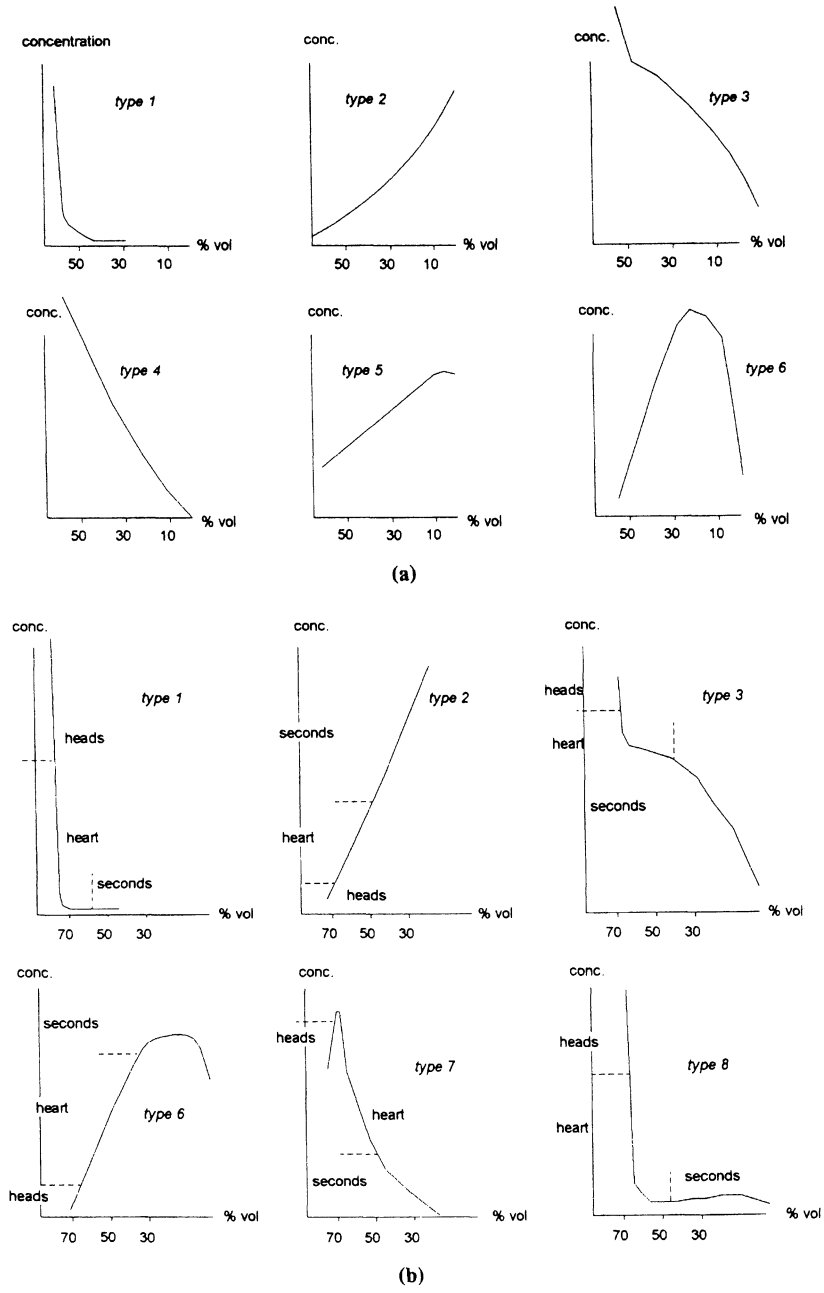
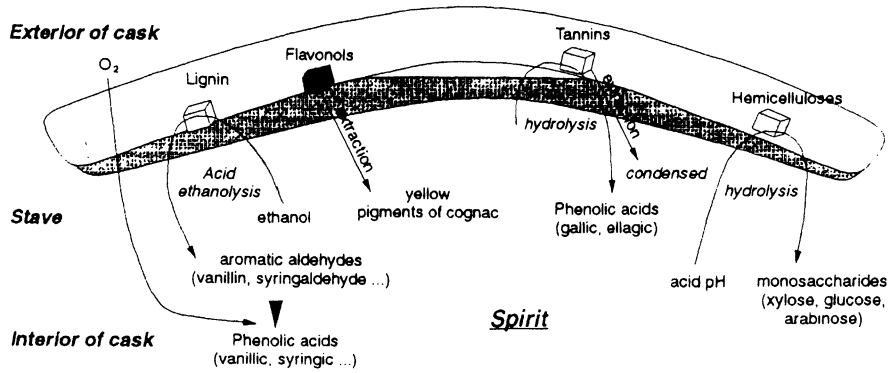
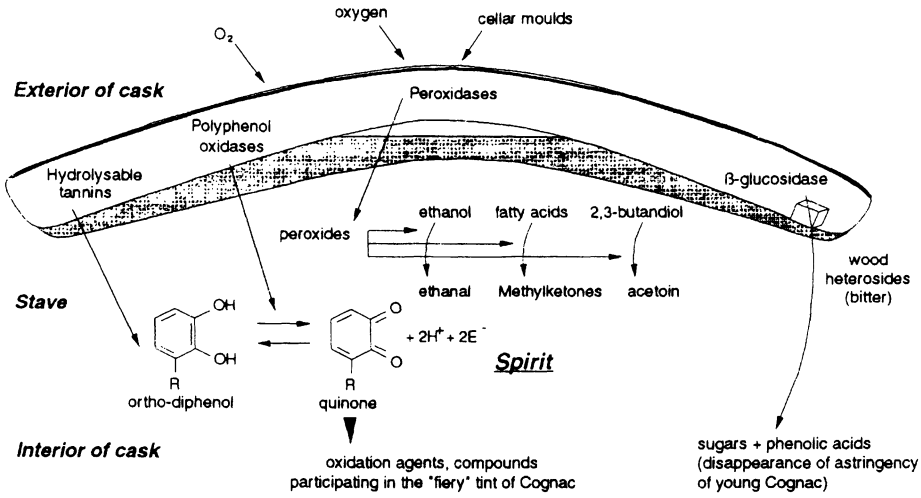


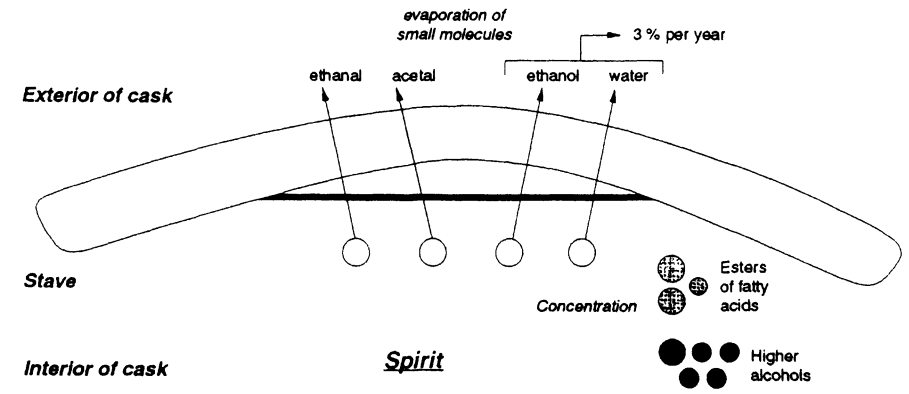
Figure 9–4 The 'passing over' of constituents of the fermentation during distillation (a) First distillation (*brouillis*). Type 1: ethanal, acetals, ethyl esters (C_2 to C_{18}), isoamyl acetate, isoamyl caprate; type 2: furfural; type 3; methanol; type 4: higher alcohols, phenylethyl acetate; type 5: 2-phenylethanol; type 6: ethyl lactate and diethyl succinate. (b) Second distillation (*bonne chaufe*). Type 1: ethanal, acetals, ethyl esters (C_2 to C_{16}), hexyl acetate, isobutyl caprate, isoamyl esters (C_2 and C_8 to C_{14}); type 2: 2-phenylethanol; type 3: methanol; type 6: furfural, phenylethyl acetate, ethyl lactate and diethyl succinate, fatty acids (C_8 to C_{12}), volatile acids; type 7: higher alcohols, ethylesters (C_{18} saturated and unsaturated); type 8: ethyl esters (C_8 and C_{10}).



(a)



(b)



(c)

Figure 9–5 Mechanisms involved in the aging of spirits. (a) Extractions; (b) chemical reactions: oxidations, hydrolysis; (c) evaporation, concentration.

Cognac has not been completely elucidated. Some mechanisms are described in Figure 9–5. Two people play an important role in this final phase of Cognac production: the cooper and the cellar master.

The cooper chooses the woods carefully. The geographical origin generally determines the fineness of the grain; for example, the oak of the forests of Allier or of Tronçais have a fine grain texture, while the Limousin oak has a coarse grain. Therefore, a spirit which is aged in a barrel of coarse-grain oak may extract 30 % more phenolic compounds and tannins than when placed in a barrel of fine-grain oak.

After splitting the wood is dried in the open air. The best results are obtained after three years of drying. The staves then have a moisture level of about 13–14 %. Each step of the construction of the barrel is important: the thickness of the staves, the size of the barrel and the intensity and duration of the charring. The heating of the barrel to shape the staves is a delicate operation. The intensity of the charring of the barrel influences the aroma of the spirits. If the charring is intense, they are richer in tannins and other compounds extracted from the wood (aromatic aldehydes, furan aldehydes, etc.) (Cantagrel *et al.*, 1992a, Puech *et al.*, 1992, 1993).

The new spirit is put into new wood for a period of about 8 to 12 months before being transferred into an older barrel known as the *roux* (tawny), in order to avoid the appearance of astringency and of marked bitter flavors.

Oak is composed of cellulose, hemicelluloses, lignin and tannins. The spirit will not only extract these elements which make up the wood but will also transform certain of them and, thus, contribute to the progressive building-up of the bouquet of aged Cognac. The aging phenomena are very dependent on the alcohol content of the spirits (Figure 9–6). Their solvating power towards the wood compounds varies as a function of the chemical family: the aromatic aldehydes such as vanillin are better extracted by a high-strength spirit (60–70 % vol.), whereas the sugars and polyols are better extracted at lower strengths (40–50 % vol.).

An overall distinction can be made between two types of flavor compound:

- those whose liberation depends only on time and which constitute a constant potential for a given variety of barrels (old or new, type of oak), e.g. vanillin, gallic acid, syringaldehyde
- those whose levels are initially governed by the coopering techniques used (e.g. intensity of charring during the making up of the barrels), which constitute a variable potential (also revealed by the passage of time) and determine the 'identity' of the barrel, e.g. furfural, coniferaldehyde and sinapaldehyde.

The quality of Cognacs arises from the harmonious equilibrium between all the constituents. Traditional observations seem to prove that this equilibrium is optimum for intermediate alcohol contents of 50–55 % vol. (Cantagrel *et al.*, 1992b).

The stave is a partition permeable to air; it permits the passage of oxygen which will cause oxidation reactions on compounds extracted from the wood and on those from the initial spirit. The enzyme complexes present in the molds of the cellars will also participate in the building up of the quality of old Cognacs. The stave also plays the role of a selective membrane towards the compounds of the spirit. It permits a slow evaporation of the smallest and most volatile molecules. The progressive losses in water and alcohol bring about a concentration of the larger molecules.

The cellar master adjusts the initial qualities of the spirits with those that can develop in the barrels using environmental factors: temperature and moisture level in the warehouse. In a dry warehouse, the evaporation is preferentially that of water and hence there is an increase in the alcohol content. In a humid warehouse, the evaporation is essentially a loss of alcohol: the Cognacs acquire more fineness, mellowness and *rancio* character.

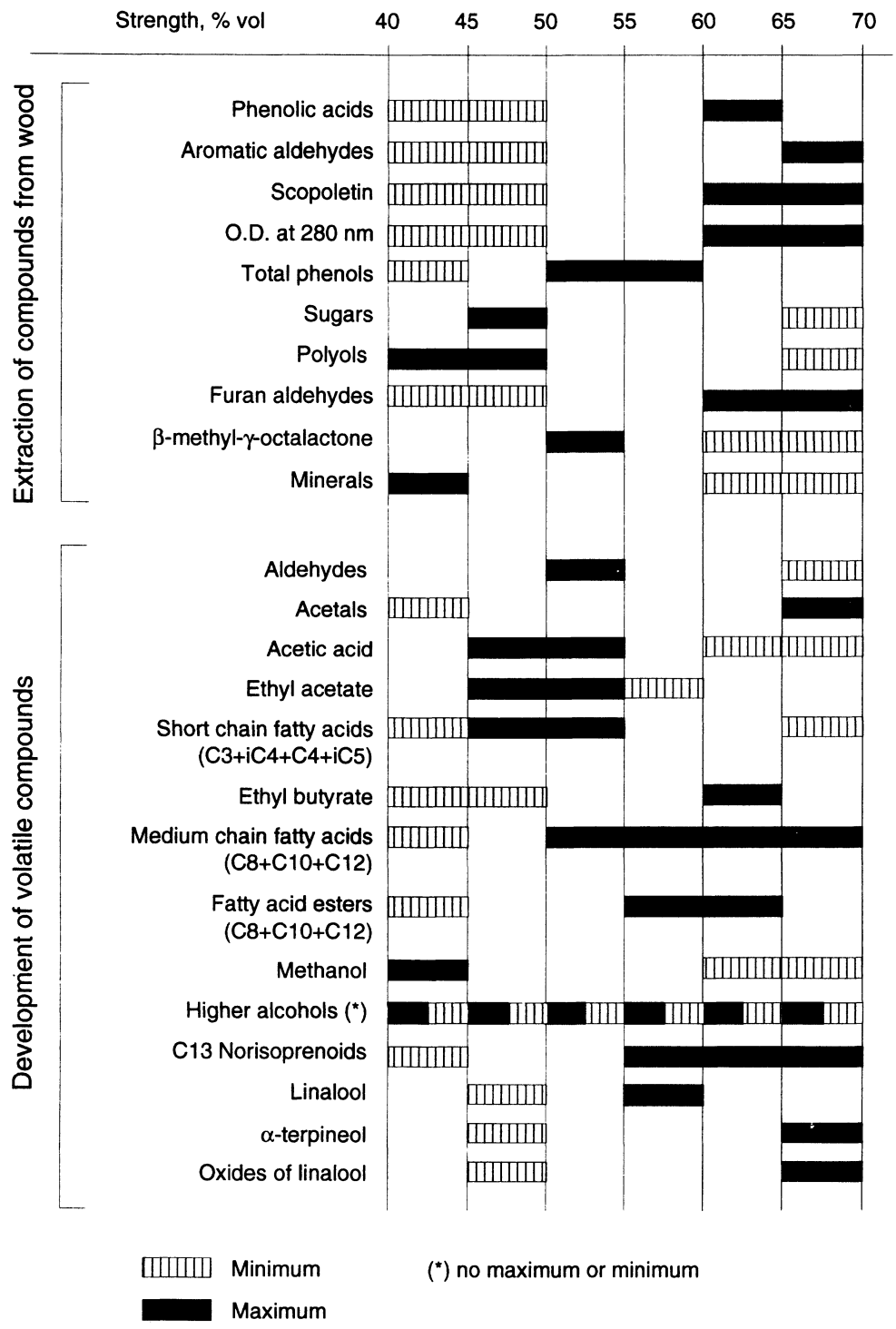


Figure 9–6 Analytical survey of spirits of different strengths during the course of aging.

BLENDING: AN IMPORTANT STEP IN THE PROCESS OF COGNAC PRODUCTION

In the general practice of Cognac production, the blending and progressive reduction of the alcohol level are carried out during the aging period so that the consumer receives a quality product in a perfectly stable chemical equilibrium (Joumier *et al.*, 1988; Cantagrel *et al.*, 1990).

The Development of the Chemical Equilibrium During Blending and Reduction

The new distillates, blended or not, have an alcohol level of about 70 % vol. The aging contributes, in general, to a progressive reduction in the alcohol level, but a final strength of 40 % vol is required for delivery to the consumer. This necessitates several steps of reduction of the spirits, since it can never be done suddenly in a single step.

To understand the development of the chemical equilibria during the phases of blending and reduction, we have analyzed each spirit making up the composition of a blend of 3-Star Cognac, as well as the resultant blend after the reduction. Seventeen spirits made up this blend in proportions of 0.1 % to 48.2 %. The average final alcohol strength before reduction was 64.3 % vol. and after reduction it was 50.4 % vol. The large percentage of spirits in this blend are intended to maintain a high stability of quality in the final product which goes on the market. In Table 9–8 the analytical results are given and the variation

Table 9–8 Evolution of chemical equilibra for the production of a blend of 3-Star Cognac (blending + reduction)

Consituent	*Absolute alcohol (real) (mg/l)*	*Absolute alcohol (theoretical) (mg/l)*	*% Variation (real/theoretical)*[a]
Acetaldehyde	88.1	76.7	+14.9
1.1-diethoxyethane	28.4	43.4	–
1.1-diethoxy-2-methyl-propane	10.5	18.4	−42.9
Ethyl acetate	500	575	−13
Ethyl propionate	3.39	3.54	−4.2
Ethyl butyrate	4.88	5.72	−14.7
Ethyl caproate	6.71	6.93	−3.2
Ethyl caprylate	31.2	32.6	−4.3
Ethyl caprate	47.2	51.6	−8.5
Ethyl laurate	26.4	28.0	−5.7
Ethyl lactate	347	357	−2.8
Isoamyl acetate	18.3	22.0	−16.8
Isoamyl caprylate	1.11	1.25	−11.2
Isoamyl caprate	2.74	2.81	−2.5
Phenylethyl acetate	4.29	4.91	−12.6
Hexyl acetate	1.27	1.46	−13
Methanol	532	493	+7.9
Propanol	403	392	+2.8
Isobutanol	895	832	+7.6
2-Methyl-1-butanol	417	396	+5.3
3-Methyl-1-butanol	2048	1977	+3.6

[a]The variation was calculated taking into account the contraction in volume during the reduction (0.92 % when the alcohol strength goes from 65 % vol. to 50 % vol.)

observed for some constituents (aldehydes, acetals, esters, alcohols) compared to the expected theoretical concentrations. A systematic increase of the principal alcohols is observed and a decrease in the esters. The esters derived from acetic acid appear to fall significantly, greater than 10 % in absolute terms:

- ethyl acetate: − 13 %
- isoamyl acetate: − 16.8 %
- hexyl acetate: − 13 %
- phenylethyl acetate: − 12.6 %

Other important variations are: acetaldehyde (+ 14.9 %) and the acetals greatly reduced (− 34.6 and − 42.9 %).

The law of mass action (large addition of water) plays an important part in the hydrolysis equilibria of esters and acetals.

$$\underset{\text{acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \underset{\longleftarrow}{\rightarrow} \underset{\text{ester}}{RCOOR'} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{aldehyde}}{RCHO} + 2\,R'OH \underset{\longleftarrow}{\rightarrow} \underset{\text{acetal}}{RC(OR')_2} + \underset{\text{water}}{H_2O}$$

For a large number of other compounds, the mixture of different products of the blend and the reduction in alcohol levels lead to a Cognac whose composition is the result of the average mixture.

Production of the Blend

The art of the cellar master consists in selecting the batches of Cognac which will make up the blend. This entails the mixing of several batches of Cognac. When working with liquids, a mixture is definitive in so far as its different components can no longer be separated. This is why the cellar master works first on samples before making up a blend. These samples are tasted, analyzed and compared to references. When the sample is finally suitable, the full-scale production can go ahead. As long as the blending is not satisfactory, each Cognac must be re-examined and tasted individually to refine the results and rectify the percentages.

A blend is not produced by accident. The cellar master has at his disposal a stock with references of quality, cru, age and price with which he will refine his blend. Tasting plays a very important role. It is the principal 'tool' of work for deciding on and carrying out the final blend, which will be bottled a few months after being made up.

Notions of Age

The spirits are followed by age class (*compte*). For example, on 31 March 2000 the classification was as follows:

Compte 00: 1999 harvest, in the course of distillation from November 1999 to 31 March 2000

Compte 0: 1998 harvest
Compte 1: 1997 harvest
Compte 2: 1996 harvest
Compte 3: 1995 harvest
Compte 4: 1994 harvest
Compte 5: 1993 harvest

Compte 00 is an intermediate class which enables the gap between the age class and the harvests to be accounted for. The age class changes on April 1st. The 1999 harvest was gathered in October 1999, and distilled during the winter of 1999–2000, no later than March 31st. *Compte* 00 disappears on April 1st. The 1999 harvest becomes *compte* 0, the 1998 harvest becomes *compte* 1, etc. The age class does not necessarily indicate the year of vintage. It is used to ensure a minimum of maturation. In a blend in which there are several Cognacs of different ages, it is the youngest Cognac which gives the age class of the blend, independent of its concentration.

Commercial Denominations

The blends are reflected in the commercial denominations marked on the labels of Cognac bottles. The commercial denomination indicates the blend, in which the youngest constituent is the determining factor. The official texts indicate for each category the minimum age of Cognac which it is possible to use (*compte* 2 for 3-Star, *compte* 4 for VSOP, *compte* 6 for Napoleon and XO).

Finally, it should be emphasized that the guarantees of quality apply only to Cognac and not to ordinary spirits produced in France or elsewhere and marketed under these same denominations.

CONCLUSION

The development of analytical techniques in the 1980s has enabled us to make a fuller study of the composition of Cognac and to better understand the role of a large number of the compounds in defining its quality. The setting up of viticultural and enological experimentation has made it possible to better understand each step of the process of production of the spirits, thus permitting the integration of new technologies.

It is the harmony between the contribution of the wood and the initial qualities of the spirits which give Cognac its distinction. Many years of maturation are necessary to obtain this harmony which makes Cognac renowned throughout the world.

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10

Armagnac and Wine-Spirits

Alain Bertrand

ARMAGNAC

Historical Background

According to scholars (Dufor, 1982; Cousteaux and Casamayor, 1985; Sempe, 1988; Roget and Garreau, 1990), Armagnac is the oldest known wine spirit; that it has been produced without interruption since the early fifteenth century has been formally established.

The name is the result of successive transformations of the word 'arminiacum', meaning owned by or estate of Arminius. Arminius could be the latinized form of Hermann, a Saxon warrior and a companion of Clovis, the Frank king, who had crossed the Rhine in 406 to wage war in the south-west of France. A Count of Armagnac is recorded in about 1032.

As in many other regions of France, the vineyards developed considerably under the Romans until their expansion was temporarily interrupted by a decree of Emperor Domicien in 92 (in fact, half of the vines were pulled up and not planted again until 267, when Emperor Probus published an edict authorizing wine growing in Gaul). Vines continued to be planted all through the barbarian invasions and developed essentially around the monasteries. A tithe levied by the monks from the Abbey of Saint Mont (Gers) testifies that wine was being produced in the tenth century.

In 1254, Bayonne was actively trading with merchants from northern Europe; wines from Chalosse and probably from the west of Armagnac were shipped down the Adour. Wines from 'Haut Armagnac' passed in transit on their way to Bordeaux, but, in 1241, the Bordeaux authorities decided to regulate, to their advantage, the Haut-Pays wines arriving in Bordeaux.

For a region so far removed from any natural outlet to the sea, distillation proved very early to be a reasonable solution, with smaller volumes to transport and without deterioration in the quality of the wine. This explains why the Comté d'Armagnac became the first region of France to develop distillation. At the time, most of Aquitaine was English and wine growing was certainly favored by the flourishing trade between England and northern Europe, as well as by the pilgrimage to Santiago de Compostela.

In 1411, the archives of the Haute-Garonne show that a distiller, M. Antoine ('aygua ardentarius') was producing a wine-spirit 'aygue de Bito' in Toulouse; 28 years later, in 1439, the

same source mentions other distillers: Jean Nouvel and his wife 'facientes aquam ardentum'. One document dated 1461 mentions the levy of taxes, which testifies to the beginning of an armagnac trade in Saint-Sever (Landes). In 1489, a document in the Gers archives mentions the presence of a still in Solomiac (Gers). By 1550, both Bordeaux and Bayonne were selling Armagnac to northern Europe.

Until the eighteenth century, wines were distilled in pot stills; these were simple devices similar to those described by Savonarole in 1440 in his treaty on distillation 'Confidencia Aquae Vitaé, in which he describes the first copper still with a coil plunged in cold water. It was only toward the mideighteenth century that distillation methods began to be improved. In 1761, with the help and advice of the chemist Chaptal, Menier invented a new process known as continuous distillation, a process patented by Adam in 1801.

This new distillation technique rapidly spread to the whole Armagnac area and is still the method used today, with very few alterations. However, the type of still used in Charentes had to gain formal approval again in 1972.

The French Revolution boosted production: 50 000 hl of pure alcohol were produced in 1810, and over 100 000 hl in 1873, corresponding to 107 000 ha of vines. At that time, the Armagnac vineyard was one of the largest in France. In 1879 it was hit by phylloxera; ten years later, alcohol production had been reduced by two-thirds. The vineyard was never to be entirely replanted and present-day production wavers between 15 000 and 20 000 hl per year.

Appellation Areas, Soils, Climate, Vine Stocks

The region of production covers about 12000 ha, divided in three areas: Bas-Armagnac, Tenareze, and Haut Armagnac (Figure 10–1). Bas-Armagnac is the most productive area—about 60 % of the vineyard—with acid, predominantly sandy soils. By comparison, the soil in Haut-Armagnac is mainly composed of calcareous clay and has virtually ceased to produce wine-spirits. A blend of wine-spirits from several minor appellations can only be called Armagnac.

Bas-Armagnac is a flat area of the edge of the Landes forest, and the slightly acid, siliceous clay soil often contains iron oxides which endow it with a dark color—hence the name 'fawn sands'. The annual mean temperature is 13 °C, with 7.5 °C in winter and 20 °C during the 3

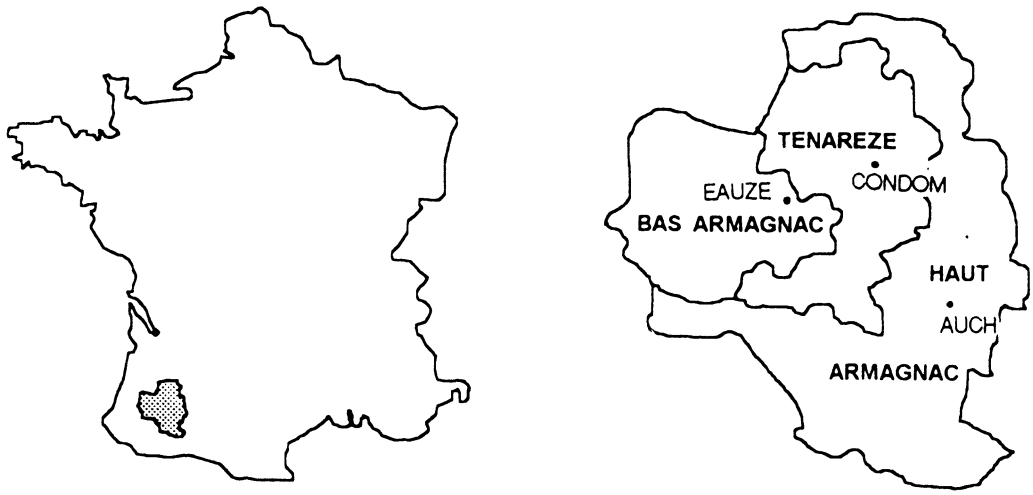


Figure 10–1 Armagnac in France and the three Appellation areas.

summer months (source: Meteo France). Annual rainfall is 892 mm. The rain is well spread out over the year, with a 1 mm minimum in July and a 86 mm maximum in May.

The hilly landscape of the Tenareze area consists of a variety of soils: sand, outcrops of calcareous clay and 'boulbenes' (a mixture of clay and fine sand) in the valleys. Being further away from the ocean, and especially from the Landes forest, the climate is a little more 'continental' entailing atmospheric disturbances and more rainfall. Mean annual rainfall is 804 mm, the main difference from the Bas-Armagnac area is the frequent thunderstorms in October. Likewise, temperatures range between 7.2 °C in winter and 26 °C in summer. This difference is caused by wind conditions, the area being still exposed to the East wind ('vent d'Autan'), which causes the end of summer drought and storms.

In Haut-Armagnac, soils are more calcareous and the climatic differences even more pronounced. The average period of sunshine in Auch is 1934 hours; surprisingly, this is 5 % less than in Bordeaux, perhaps because of a longer period of cloud cover.

The different vine stocks allowed are Ugni blanc, Baco 22 A, Folle Blanche and Colombard. Ugni blanc, an Italian vine stock related to Trebbiano, is rapidly gaining ground as it offers the advantage of coming to maturity in the '3eme epoque' (45 days after Chasselas maturation), thus eliminating the problem of rot, and it produces low-alcohol wines suitable for distillation. Baco 22 A, which ranks second for making Armagnac, is a hybrid of Noah (v. labrusca × v. riparia) and Folle Blanche; it matures 30 days or more after Chasselas ('maturite de 2eghyme epoque'), is very diseasehardy and does not require grafting thanks to the sandy soil of the Landes. This variety stands out as an exception among the vinestocks used for French Appellations d'Origine Controlees. The Institut National des Appellations d'Origine des Vsins et Eaux-de-Vie (INAO, the French National Institute For Wine and Spirits Appellations of Origin) is planning to eliminate it from the Armagnac vineyard by 2010. The rather 'foxy' flavor of Baco wines caused by the presence of furaneol and methyl anthranilate ('labrusca' character) disappears during distillation and neither substance is detectable in the spirits.

The vineyards are of average size; pruning is managed according to the Guyot method in one or two stages; the vines are trellised and there are 4000 to 5000 vines/ha.

Vinification

Most vinegrowers use a grape harvester to harvest the grapes and a continuous wine press to extract the juice; such methods, which are usually too brutal for immature grapes, have no particular drawbacks in this case as long as the marc is not strained too much.

The temperature of alcoholic fermentation is rarely checked. Wines are not subjected to any oenological process, and sulphur dioxide is strictly forbidden (Decree of 6 August 1936, modified 24 May 1956). Wine alcohol concentration varies considerably, ranging between 8 and 11.5 % vol. or more; acidity is average (4 to 6.5 g/l expressed as H2SO4). Malo-lactic fermentation usually occurs spontaneously just after alcoholic fermentation.

According to the Bureau Interprofessionnel de l'Armagnac (BNIA), 60922 hl of pure alcohol were distilled in 1990 from 567 000 hl of wine. Production in 1993 was particularly good. The average yearly production is about 40 000 hl 100 % vol. alcohol.

By law, wines have to be analyzed in an appointed laboratory to prove they are free of sulphur dioxide and of sufficient quality to be used to make Armagnac.

Distillation and Regulations

Wines have to be distilled in the Appellation area. Two sorts of stills are used; the BNIA has listed the following ones in use:

- 132 continuous stills, 'Armagnacais'
- 22 pot stills, producing less than 10 % of the total volume of Armagnac.

The maximum distillation alcohol concentration allowed is 72 % vol., the same as other

French AOC wine-spirits (Decree of 6 August 1936). The minimum for white spirits (when they come out of the still) is set at 52 % vol.

Wines are required to be distilled between the end of the harvest and the 31st March of the following year (Decree of 15 March 1988, modified) (BNIA).

The Continuous Armagnac Still (Figure 10–2).

The continuous still used in Armagnac is made entirely of annealed electrical grade copper; it works very much like steam-entrained distillation and plays an essential role in the specificity of Armagnac.

The boilers, distillation columns, wine-heater and cooler constitute the still's main parts. The volume of the boiler ranges from 5 hl to a maximum of 35 hl; it is divided into two or three sections by separation plates. The total capacity of the boilers must be at least equal to that of the cooling unit, which includes the wine-heater and the cooler. The wine is always heated over an 'open fire', usually propane gas although wood is still frequently used to heat small stills.

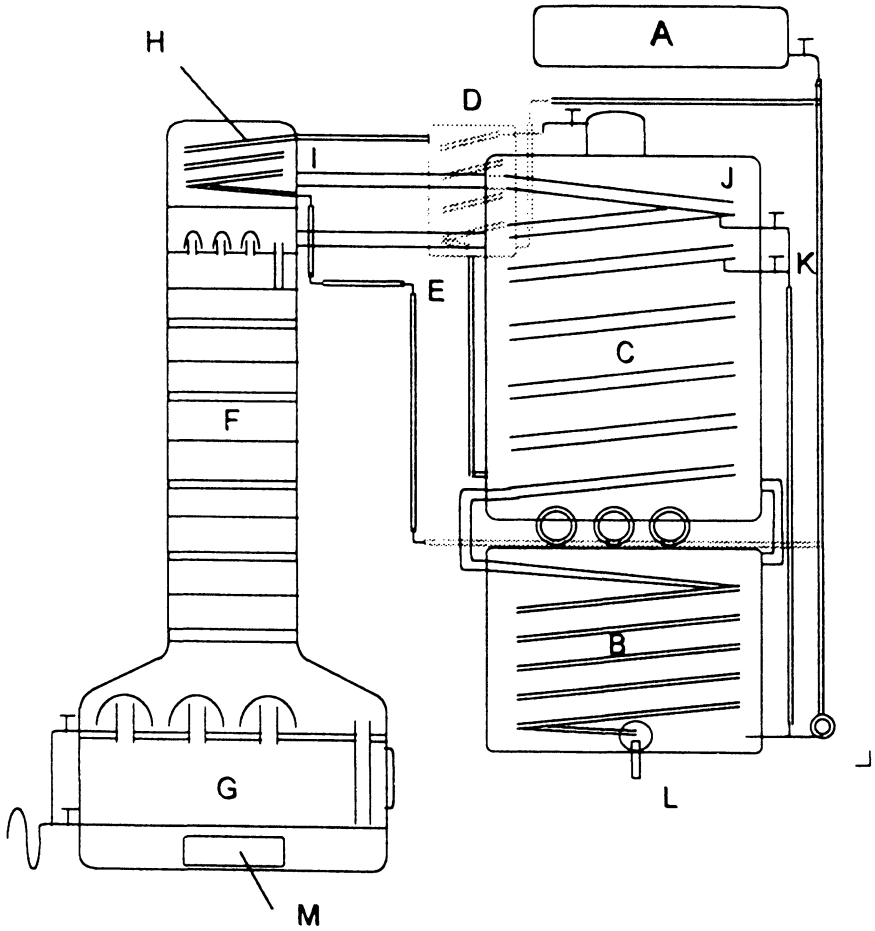


Figure 10–2 Armagnac still. A: head of wine; B: cooler; C: wine heater; D: head condenser; E: wine arrival; F: column; G: boilers; H: head column coil; I: swan neck; J: coil; K: drawing and recycling of tailings; L: alcoholmeter holder; M: furnace.

The column has 5 to 15 plates (the most recent stills have about 12 plates). These plates are fitted with different shape bubble-through devices: bubble caps, bell-shaped. The plates above the wine arrival pipe are called 'dry plates' and help reduce tailings while increasing the alcohol concentration.

The wine-heater is used to preheat the wine, the coil inside bringing the temperature up to 70 or 85 °C, which condenses the alcoholic vapors issuing from the column. The capacity of the wine-heater varies considerably (5 to 15 hl).

The cooler, which is generally smaller (3 to 10 hl) than the wine-heater, is placed under the latter. After going through the wine-heater, the coil goes into the cooler to achieve complete condensation and cooling of alcoholic vapors.

Sometimes, a head-foreshots condenser system can be fitted to the still above the wine-heater; more frequently though, a tail-products condenser is placed level with the alcoholic vapor pipe, between the column and the wine-heater. Tailings can also be collected in the first turns of the coil. The condensed fractions can be returned to the wine and recycled. A coil can be added to the head of the column, to circulate preheated wine in the head or tailings condensers; this also helps to condense the least volatile products and to increase the percentage of alcohol.

The wine from the loading vat goes into the still, at the bottom of the cooler, by gravity. The flow is regulated with a gate valve equipped with a flowmeter. The spirits come out of the still through the alcoholmeter holder where the temperature and alcohol concentration of the distillate are measured. Washy wines are evacuated continuously through a syphon connected to the boiler.

Because of the way it works, Armagnac distillation is not only far more economical than two-stage distillation but also three times as fast. The daily quantity produced cannot exceed one and a half times the capacity of the whole cooling system.

When it has been running for about 2 weeks, the still is turned off and cleaned. Sediments accumulated on the plates and residues prevent the copper from fixing the volatile acids and sulphurous compounds. Inadequate cleaning soon results in the appearance of an unpleasant flavor and a greasy rancid smell, like 'seconds'.

To start the still the boiler and the column are filled with water; once the wine-heater and the cooler are full of wine, the fire is lit; when the water begins to distill, the wine inlet pipe is opened. As soon as the desired alcohol concentration is reached (60 % vol. for instance), the spirits are recovered.

With the Armagnac distillation method, the volatile substances are either entirely distilled (higher alcohols), or are more or less rectified (2-phenyl ethanol, ethyl lactate, 2,3-butanediol), according to their polarity (Wildbolz, 1986). The fatty acid ethyl esters and fatty acids with a high molecular weight are released by heating the yeasts, which means that the quantity of these acids depends on the wine's yeast content; generally speaking, there are about four times fewer fatty acid ethyl esters with 8, 10 and 12 carbon atoms in armagnac than in cognac. This leads connoisseurs to claim that the quality of armagnac comes from the specific nature of its soils and the aromas of vines harvested at maturity and not only from their yeast esters content (Table 10–1).

To modify the composition of the spirit, the distiller can control mainly two parameters: wine flow and heating. The way the still is adjusted plays an essential role in the composition of the spirits: lowering the heating or increasing the wine-flow brings down the temperature at the head of the column and results in a higher alcohol concentration; in this case higher alcohol and ester concentrations exactly correspond to the percentage of alcohol, in other words the quantity of these substances expressed in g/hl remains constant (Figure 10–3). Conversely, the amount of substances called 'tailings', of which there is usually a surplus in Armagnac, decreases exponentially when the percentage of alcohol increases (Jadeau, 1987; Bertrand, 1989a). For prolonged aging, a large quantity of tailings is an advantage because of the 'winey' character of their molecules; but if the armagnac is to be mar-

Table 10–1 Distillation of volatile substances (averages from 50 wines and their corresponding spirits)

	Wine (mg/l)	*Spirit (mg/l)*	*Recovery (%)*
Ethanol, % vol.	11.1	59.7	
Higher alcohols	373	2043	102
Methanol	41.4	194	87
2-Phenyl ethanol	53	32	10
Higher alcohol acetates	2.61	12.7	90
Volatile acid ethyl esters	1.46	14	177
Ethyl acetate	41	207	94
Diacetyl	0.65	2.91	83
Volatile acids (C3-iC5)	4.12	10.79	38
Volatile acids (C6-C12)	11.2	34.2	56
Ethyl lactate	340	248	14
Acetic acid	400	118	5.5
2,3-Butanediol	549	14.9	0.5

keted rapidly, it is preferable to make a high-proof distillate to limit the amount of such substances.

Two-Stage Pot Stills

These stills are used in the same way as in Cognac; however, in Armagnac, sediments are never re-introduced in suspension into the wine before distillation. Two-stage distillation has its advantages, as the Armagnac ages more quickly and can, therefore, be marketed much earlier, although it loses some of its specificity in the process.

Analysis

Two sorts of analyses are carried out on wine-spirits: the traditional ones, and analyses to improve knowledge of the products and establish correlations between their chemistry and organoleptic observations.

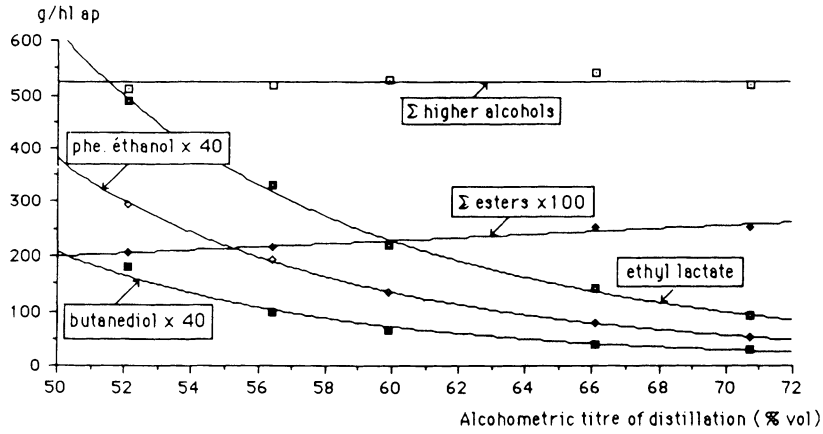


Figure 10–3 Variation of volatile substances during continuous distillation with the Armagnac still as a function of the alcoholic titre.

Traditional Analyses

These are used to determine real and raw volume percentages of alcohol (titration), dry extract, total acidity and the ratio of non-alcoholic elements, i.e. volatile acids, aldehydes, esters, furfural and higher alcohols; methanol values are determined separately.

Table 10–2 shows some mean values for the two French AOC wine-spirits compared with those of brandy. The non-alcohol coefficient of brandy is noticeably lower than the others; this is because it is produced in columns. Conversely, brandy contains more methanol than Armagnac or Cognac, because it is made essentially with red wines.

Gas Chromatography

This is used to analyze volatile compounds. As an example, the chromatogram in Figure 10–4 shows some of the volatile alcohols, esters, acids, and various aromatic components contained in an ether-hexane extract of VSOP Armagnac. Other analyses can be carried out by injecting the spirits directly into the chromatograph. The high levels of butanediol found in Armagnac show that it is rich in tail products. A set of average values can be established from these analyses (Table 10–3).

High-Pressure Liquid Chromatography (HPLC).

Different wavelength HPLC analyses can also be carried out by absorption spectroscopy to measure the principal phenolic compounds extracted from wood which contribute to the vanilla flavor that develops with age.

Sensory Analyses

Effective analyses can also be carried out by experienced winetasters. Tasters fill in a multiple choice question tastingcard and tick off the boxes corresponding to their perceptions; there are also questions related to 'hedonistic' sensations. Since Armagnac comprizes several hundreds of

Table 10–2 Classical analysis of wine spirits

	Armagnac		*Cognac*		*Brandy*	
	X	*S*	*X*	*S*	*X*	*S*
Alcohometric titre at 20 °C						
Real (% vol.)	41.4	1.6	40.34	0.75	45.46	11.1
Brut (% vol.)	40.13	2.3	38.72	1.1	43.64	11.6
Dry extract (g/L)	4.5	3.5	6.7	3	8.43	1.58
Total acidity as acetic acid (g/L)	153.9	57.6	103.6	28.2	31.46	0.23
Volatile acidity as acetic acid[a]	106.5	37.5	59.3	19.3	19.06	3.53
Total aldehydes as ethanal[a]	23.3	6.4	19.3	8.25	25.33	7.32
Total esters as ethyl acetate[a]	109.6	34.7	72.9	7.2	54.8	6.72
Ethyl acetate	76.3	24	45.3	5.9	38.5	4.2
Furfural[a]	1.2	0.3	2.45	0.93	0.35	0.14
Total higher alcohols[a]	441.4	42.3	444.4	127.5	258.4	23.28
2-Butanol	0.5	0.85	0.7	1.6	3.39	1.64
1-Propanol	49.4	13.5	43	7.8	25.06	2.22
2-Methyl-1-propanol	104.5	19	121.7	15.8	55.43	5.09
1-Butanol	0.2	0.5	0.1	0.3	1.34	0.67
2-Methyl + 3-Methyl-butanol	286.6	33.2	312.3	29.6	172.73	20.46
Total volatile substances	682.1	83.6	632	42.2	357.5	31.36
Methanol	47	10.9	49.7	11.4	69.2	16.5

Results as g/hl pure alcohol, if no other indication; X, average (15 representative samples); S, standard deviation.
[a]For the sum of volatile substances.

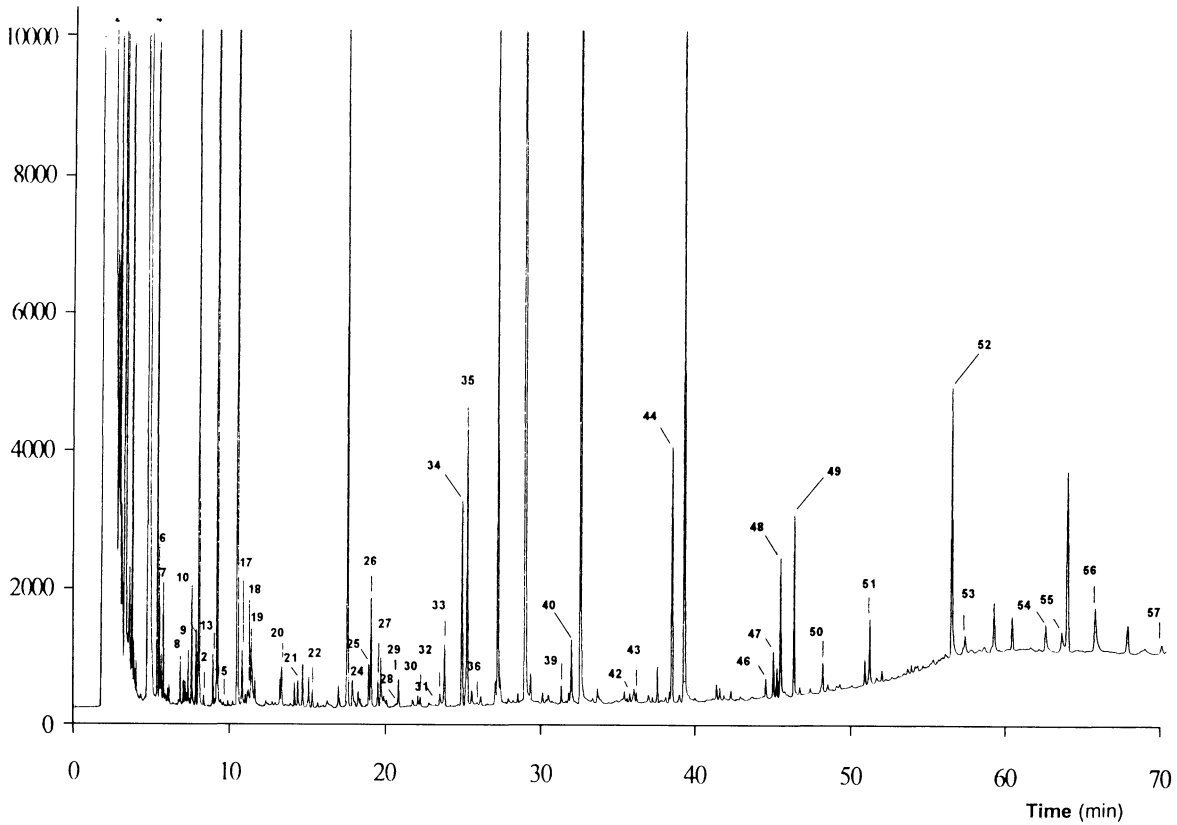


Figure 10–4 Chromatogram of the extract of a VSOP Armagnac by ether hexane (concentration about 10 times); column FFAP 50 m, 0.22 mm; splitless injection; temperature programme from 50 ° to 200 °C. Identification of the peaks: 1, Ethyl butyrate; 2,2-methyl-l-propanol; 3, isoamylacetate; 4, isoamyl alcohols; 5, ethyl hexanoate; 6, hexyl acetate; 7, styrene; 8, acetoin; 9, ethyl heptanoate; 10, ethyl lactate; 11, 1-hexanol; 12, *trans*-3-hexen-l-ol; 13, *cis*-3-hexen-l-ol; 14, 3-octanol (internal standard l); 15, *trans*-2-hexen-l-ol; 16, ethyl octanoate; 17, *trans*-linalol oxide (furane); 18, *cis*-linalol oxide (furane); 19, acetic acid; 20, benzaldehyde; 21, linalol; 22, 2-methyl propionic acid; 23, ethyl decanoate; 24, butyric acid; 25, 3-methyl butyric acid; 26, diethyl succinate; 27, α-terpineol; 28, 1,1,6-trimethyl l-dihydronaphthalene (TDN); 29, methionol; 30, citronellol; 31, nerol; 32, damascenone; 33, phenylethyl acetate; 36, ethyl dodecanoate; 35, hexanoic acid; 36, benzyl alcohol; 37, phenyl-ethanol; 38, heptanoic acid (internal standard 2); 39, 4-ethyl guaiacol; 40, ethyl myristate; 41, octanoic acid; 42, 4-allyl guaiacol (eugenol); 43, 4-ethyl phenol; 44, ethyl palmitate; 45, decanoic acid; 46, ethyl stearate; 47, ethyl oleate; 48, lauric acid; 49, ethyl linoleate; 50, ethyl linolenate; 51, myristic acid; 52, palmitic acid; 53, palmitoleic acid; 54, stearic acid; 55, oleic acid; 56, linoleic acid; 57, linolenic acid.

Table 10–3 Volatile substances of young Armagnacs

	Average	*Standard deviation*	*Minimum*	*Maximum*
Alcohols				
Methanol	41	10.4	24.6	58.3
1-Propanol[a]	28	4.2	19.8	32.9
2-Methyl-l-propanol[a]	98.2	18	76.2	120
2-Methyl-l-butanol[a]	47.7	3.6	42.2	52.2
3-Methyl-l-butanol[a]	216	24	185	254
1-Butanol[a]	0.81	0.28	0.34	120
2-Butanol[a]	n.d.			
Allylic alcohol[a]	n.d.			
Sum of higher alcohols[a]	391	38.8	340	436
Hexanol	10.9	2.4	6.6	13.2
2-Phenyl ethanol	25.2	6	18.2	33.5
2,3-Butanediol D(−)	8.71	2.62	6.38	13.5
2,3-Butanediol *meso*	2.66	0.92	135	4.1
Sum of butanediols	11.4	3.45	7.73	17.6
Carbonyl compounds				
Ethanal	12.9	7.7	5.11	27
Acetal	16.1	5.6	8.79	24.5
Acetol	1.02	0.14	0.84	1.22
γ-Butyrolactone	1.76	0.86	0.67	2.78
Acetoin	0.54	0.17	0.39	0.89
Diacetyl	2.72	0.99	2.27	3.9
2,3-Pentanedione	0.59	0.13	0.36	0.72
Acids				
Acetic acid	148	30	117	187
Propionic acid	0.75	0.27	0.42	1.36
Isobutyric acid	1.72	0.47	1.2	2.68
Butyric acid	1.75	0.56	0.71	2.55
Isovalerianic acid	1.62	0.57	1.07	2.5
Sum of volatile acids (Ce−*i*C5)	5.84	1.17	4.72	8.18
Hexanoic acid	2.39	132	1.16	5.32
Octanoic acid	10.35	3.28	5.76	14.4
Decanoic acid	5.21	1.56	3.39	8.02
Dodecanoic acid	0.64	0.33	0.25	1.17
Sum of volatile fatty acids	18.59	5.44	10.7	25.6
Esters				
Ethyl acetate	189	81	97	335
Isoamyl acetate	3.16	2.43	1.37	7.32
Hexyl acetate	0.11	0.07	0.02	0.19
2-Phenylethyl acetate	0.39	0.31	0.12	0.91
Sum of higher alcohol acetates	3.59	2.81	1.52	8.42
Ethyl butyrate	0.65	0.15	0.45	0.91
Ethyl hexanoate	1.71	0.29	1.36	2.09
Ethyl octanoate	3.41	0.64	2.69	4.54
Ethyl decanoate	4.08	2.64	1.47	8.04
Ethyl dodecanoate	2.66	2.2	0.54	6.52
Sum of volatile acids ethyl esters (without ethyl butyrate)	11.86	5.68	6.1	21.1
Diethyl succinate	5.31	3.45	1.68	11.1
Ethyl lactate	115	27	75	158

Results as mg/L; [a]Results g/hl pure alcohol; n.d. not detected. From Bertsch (1992).

substances, it is extremely difficult to accurately describe it in just 20 questions (which is a maximum), but no other solution is forthcoming. The tasting-card shown in Figure 10–5 is of the kind that could be used for armagnac. Results are often computer processed using multidimensional analysis methods, multiple correspondence factorial analysis being the best suited (Segur, 1988; Bertrand, 1989b; Bertrand and Segur, 1990).

The main features of old Armagnac are their aroma of prunes, their 'rancio' and their complexity; they are vigorous and even rough, with a long-lasting palate.

Analysis of Principal Ions in Armagnac Spirits

Despite much research work, unpleasant tastes still occur which have not yet been clearly explained. Recent work has studied chloride, succinate, sulphate and oxalate ions in Arma-

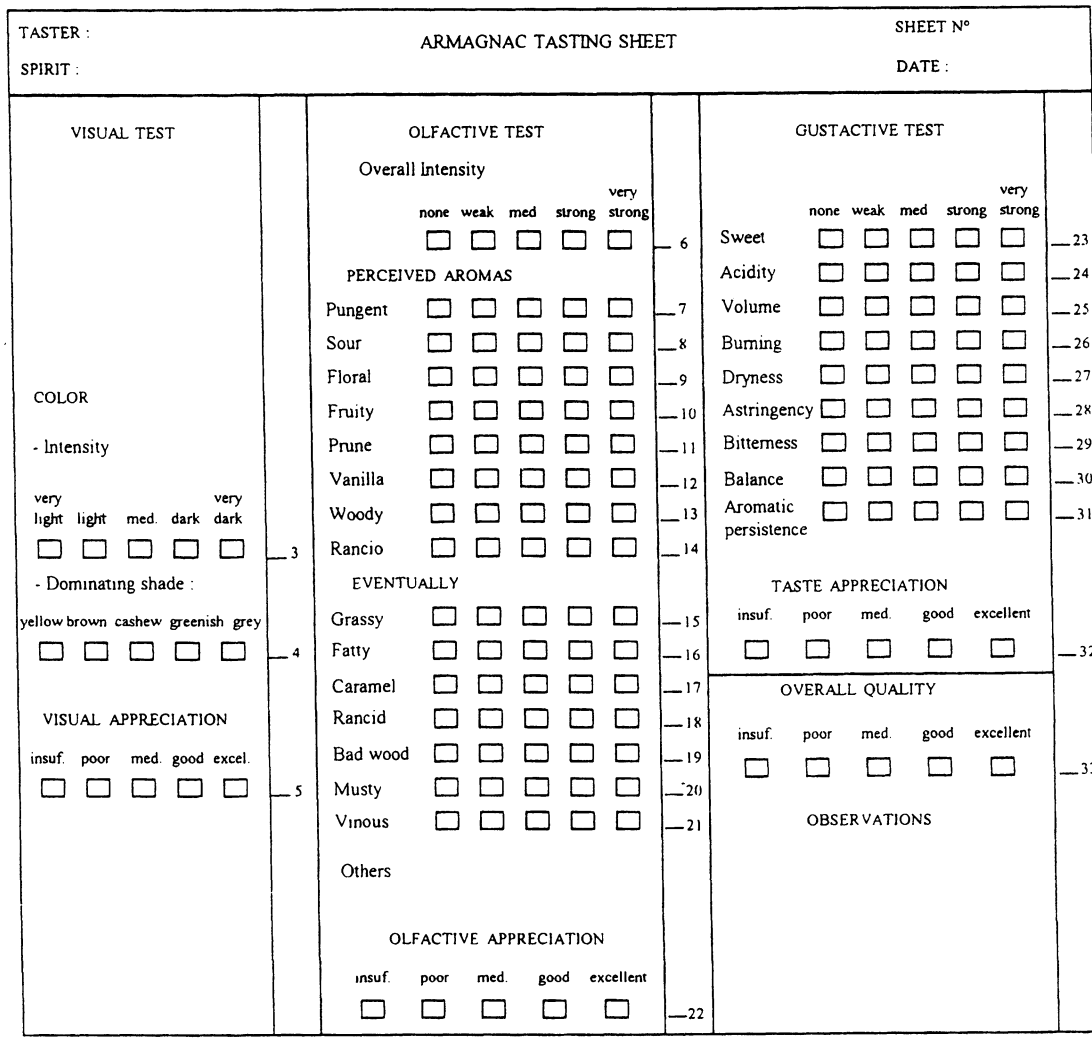


Figure 10–5 Tasting sheet for Armagnac.

gnac spirits and their contribution to some of these unpleasant characters. The sulphate content rises progressively during the aging of wines by oxidation of sulphur dioxide used as preservative. However, it is forbidden to add sulphur dioxide to grape juices in the production of Armagnac and Cognac because the ethanal, which is normally bound to SO_2, could give rise to a very pungent character in the spirit. SO_2 may be used in wine for Cognac only after fermentation and in low quantities < 20 mg/L in order to prevent oxidation, especially for the transportation of the wine (Galy *et al.*, 1992). Succinate comes from the hydrolysis of the diethyl succinate present in spirits. Oxalate is formed by oxidation of glyoxal during the aging process (Vanderlinde, 1995).

Triangular tests were performed at the following concentrations: 1, 3 and 5 mg/l of succinic acid; 50, 80 and 100 mg/l of sulphuric acid and 20, 30 and 40 mg/l of oxalic acid in aqueous ethanol, and at the same concentrations (respecting the proportions found in the spirits) of sulphate and oxalate in spirits. Chloride or succinate in aqueous ethanol were not detected at these concentrations; the sulphates gave a very unpleasant sensation of burning late on the palate, and for oxalate the sensation was dryness. Neither sulphate nor oxalate were well identified when they were added to the control spirit, because they caused a long-lasting burning sensation that made it difficult to recognize the samples.

The concentrations, determined by HPLC, of chloride and succinate in the distilled spirits were low compared with sulphate and oxalate (Table 10–4). Succinate and oxalate concentrations (Figure 10–6) increased with the age of the spirit. At the levels found in spirits, chloride and succinate were neither identified nor associated with defects in tasting. On the other hand, sulphate and oxalate imparted a very unpleasant burning sensation. This sensation is very difficult to quantify, probably due to a cumulative effect.

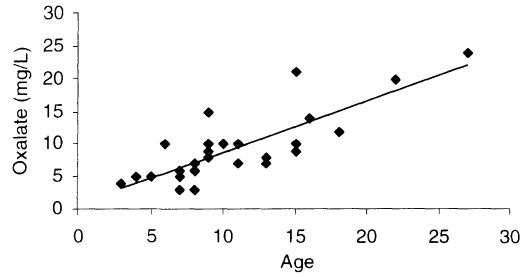


Figure 10–6 Oxalate levels as function of age of spirit.

Carbonyl Compunds in Wine Spirits

Long-chain aldehydes seem to be specific to armagnac; methyl ketones, glyoxal and methyl glyoxal levels increase with age. These carbonyl compounds contribute to the 'rancio' character of old wine-spirits. Their presence in wines and spirits was highlighted long ago (Marché and Joseph, 1975) but at high levels they can cause an off-flavor and diminish the quality of wine and distilled spirit. For instance, *trans*-hex-2-enal at very low doses seems to contribute positively to the taste of some fruit juices. However, at high levels, this aldehyde always induces a negative effect, especially with orange juice (Moshonas and Shaw, 1986). According to Dufour (1988), *trans*-non-2-enal is the main substance responsible for the cardboard taste appearing in beer dur-

Table 10–4 Concentration of chloride, succinate, sulphate and oxalate ions in Armagnac spirits (mg/L)

	Chloride	*Succinate*	*Sulphate*	*Oxalate*
Minimum levels	0.76	0.33	0.31	2.90
Maximum levels	15.0	5.08	173	26.9
Average levels*	3.59	1.26	21.5	10.8

*Average of 30 samples.

ing the aging process. According to Moll and Moll (1990) and Drost *et al.* (1990), its perception threshold by addition is 0.1 µg/l.

Aldehydes and ketones have been analyzed by gas chromatography according to the method used for wine by de Revel and Bertrand (1993) and Vanderlinde *et al.* (1992) with an electron capture detector (Figure 10–7) or a mass spectrometer (Figure 10–8). The perception thresholds in water and aqueous ethanol are shown in Table 10–5. The saturated aldehydes with an even number of carbon atoms had lower perception thresholds than those with an uneven number. Among the aldehydes which are normally considered as off-flavor agents, octanal had the lowest perception threshold (0.7 µg/l). Octanal and decanal had a characteristic orange-like smell which was considered pleasant by the tasters. The perception thresholds of the unsaturated aldehydes, which have an unpleasant smell, decreased as their carbon chain length increased. In 40 % aqueous ethanol, perception thresholds were 140 µg/l and 15 µg/l for the saturated and unsaturated aldehydes respectively. The perception thresholds of the ketones in a water solution was higher than in spirits, with the exception of heptan-2-one and nonan-2-one. Some aldehyde perception thresholds in spirits are shown in Table 10–6. The difference thresholds were higher than the highest found in the spirits analyzed. Results of olfactory sensory analysis are very close to those obtained by retronasal olfaction.

During aging in oak casks, slow but important changes in the chemical composition occur in spirits. This is especially due to the extraction of compounds from the wood and also to progressive oxidation induced by the permanent presence of dissolved oxygen. The determination of aldehydes and ketones in brandies has led to the determination of the furanic and phenolic aldehydes provided by wooden casks, as well as numerous

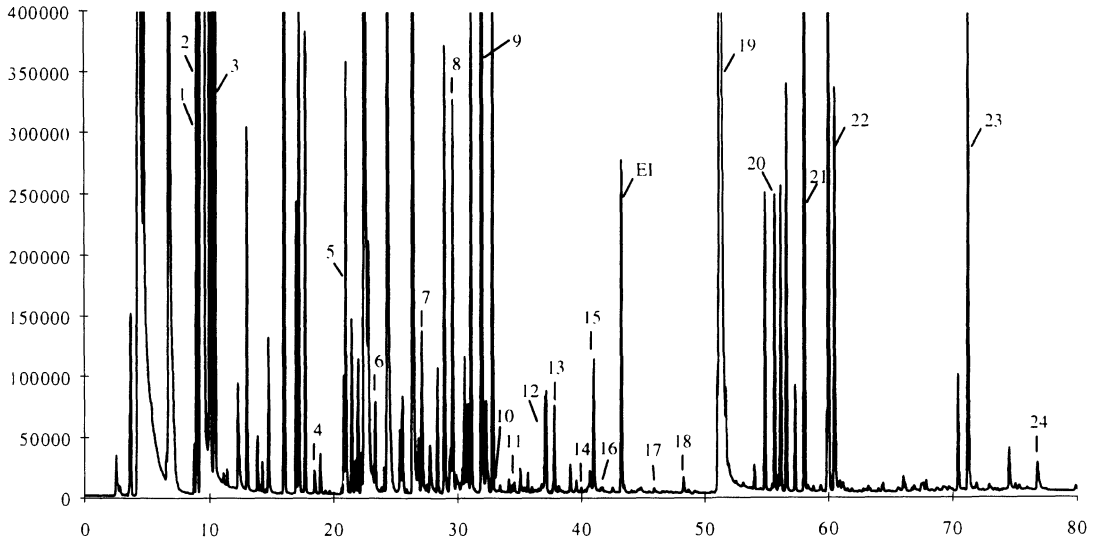


Figure 10–7 Chromatogram of carbonyl compounds of a wine spirit derived by PFBOA. Chromatographic conditions: apolar column (CPSIL 5CB 15 m × 0.32 mm × 0.12 µm); injector and ECD temperatures: 250 °C; oven temperature: 60 °C programmed at a rate of 3° C/min to 220 °C; final step: 30 min.; splitless time; 30 s. 1, propanal; 2, *trans*-prop-2-enal; 3, butan-2-one; 4, butanal; 5, 2-methylbutanal; 6, pentanal; 7, *trans*-pent-2-enal; 8, hexanal; 9, furfural; 10, *trans*-hex-2-enal; 11, heptanal; 12, 5-methylfurfural; 13, *trans*-hept-2-enal; 14, octanal; 15, benzaldehyde; 16, nonan-2-one; EI, lindane (internal standard); 17, nonanal; 18, *trans*-non-2-enal; 19, 5-(hydroxymethyl)furfural; 20, glyoxal; 21, methylglyoxal; 22, vanillin; 23, syringaldehyde; 24, coniferaldehyde.

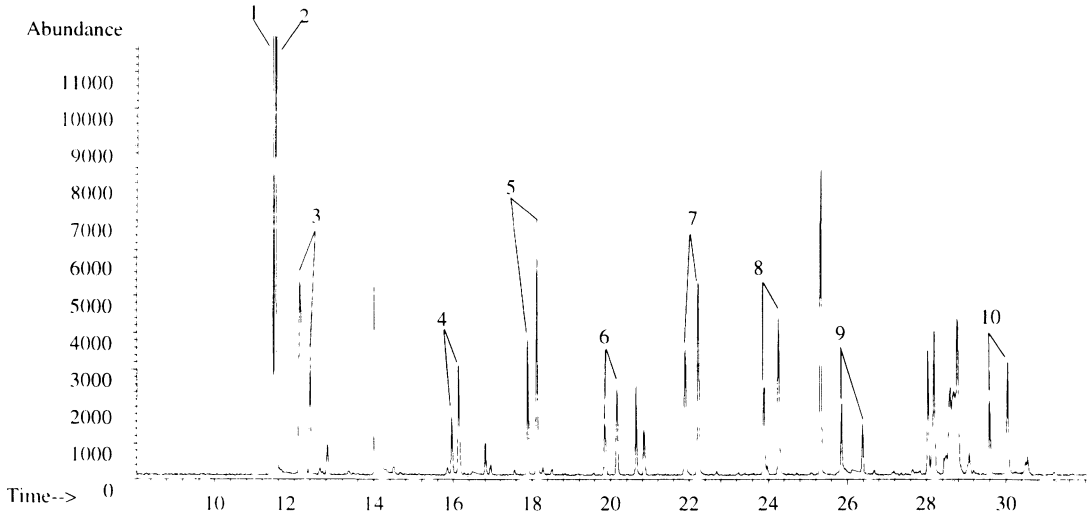


Figure 10–8 Ketones derived by PFBOA in a wine spirit. For chromatographic conditions see Figure 10–7, with the exception of detection: MS, Characteristic Ion: (M/Z = 253). 1, Acetone; 2, pivalaldehyde (internal standard); 3, propanal; 4, hexan-2-one; 5, heptan-2-one; 6, octan-2-one; 7, nonan-2-one; 8, deca-2-one; 9, undecan-2-one; 10, tridecan-2-one.

aliphatic carbonyl and dicarbonyl compounds. Some of the latter increase regularly during aging through oxidation of various precursors.

Glyoxal and methylglyoxal could come from their corresponding alcohols (acetol and propan-1,2-diol) (de Revel, 1992), but glyoxal could be also formed by direct oxidation of sinapaldehyde, which is particularly abundant in new oak barrels (Figure 10–9). Both aliphatic aldehydes and ketones are known to originate from the oxidation and peroxidation of unsaturated fatty acids. For instance, oleic acid gives octanal, and linoleic acid leads to *trans*-non-2-enal. The complexity of the chromatograms obtained is generally closely linked to the age of the spirit (Figure 10–10).

A quantitative study was performed on a panel of 54 Armagnac spirits of various origins aged from 2 to 25 years. The technological parameters of aging, especially with regard to the use of new oak barrels and duration, varying from 0 to 5 years, were very different from one producer to another. Results confirmed that the amounts of the well-known compounds directly extracted from wood, such as vanillin, depend essentially on the time spent in new barrels (Puech, 1990). However, other substances such as carbonyl compounds are also well correlated with the age of the samples. Among the aliphatic aldehydes, ethanal is known to arise from the chemical oxidation of ethanol during aging. A very wide range of ethanal concentrations may be found in young spirits due to the fermentation conditions (presence of a low quantity of SO_2 or not, enzymatic oxidation of ethanol before distillation, etc.). Butanal and 3-methylbutanal, which are probably produced by oxidation of the corresponding higher alcohols, show better correlation coefficients between concentrations and age, r = 0.56 and r = 0.71 respectively (Figure 10–11). Other aliphatic aldehydes such as pentanal (r = 0.61) and hexanal (r = 0.81) could arise from the oxidation of unsaturated fatty acids (Figure 10–11). Among the other carbonyl compounds, good correlation coefficients with age have been obtained for benzaldehyde (r = 0.66) and glyoxal (r = 0.85) (Figure 10–12). On the other hand, the level of these two compounds seems to be greater when new barrels are used during the first years

Table 10–5 Perception thresholds determined for some aldehydes and methyl ketones

Substances	Thresholds (µg/l)		Flavors
	Water	Alcohol 40%	
Methylglyoxal	3500	8000	butter
2-Methylpropanal	3.5	4200	vegetal, butyric
3-Methylbutanal	11	120	dirty foot, putrefaction, cheese
Hexanal	5	250	green leaves
Heptanal	15		vegetal*
Octanal	0.7	17	orange
Nonanal	15		rancid, astringent*, bitter*
Decanal	5		orange
trans-Hex-2-enal	40	478	bug, green leaves*
trans-Hept-2-enal	6		bug
trans-Oct-2-enal	5		lemon
trans-Non-2-enal	0.1	11	bug, papery, mushroom
Heptan-2-one	100	1200	rancid, walnut*, hops*
Octan-2-one	45		spicy*
Nonan-2-one	1.2		rancid
Decan-2-one	40		floral*
Undecan-2-one	14		vegetal*

*MBAA (1991).

of aging (Figure 10–13). New wood seems to provide both the catalysts for the oxidation reactions and the precursors of these compounds (Hervé, 1996). Carbonyl compounds do not seem to be responsible for spirit aromas. Their content in the various spirits analyzed was almost always lower then the perception thresholds, either individually or when mixed. However, the aldehydes present a burning taste, green plant flavors or rancid odors when they occur in high concentrations. The result is that the taster experiences an unpleasant sensation of burning and tiredness. The determination of various carbonyl compounds, including compounds released by the wood, in a panel of Armagnac spirits of different ages and origins has led to the identification of various aging markers. Consequently, these may be used for quality control and to optimize aging.

Aging and Merchandising Preparation

Wine-spirits are usually aged in oak casks. Coarse-grained wood is preferred (Gascony or Limousin) to fine-grained wood, as it is slightly

Table 10–6 Odor difference threshold for some aldehydes

	Initial concentration in spirits (µg/l)	Difference threshold (µg/l)	
		Olfactory test	Tasting test
Methylglyoxal	1240	10000	10000
Glyoxal	39	9000	12000
2-Methylpropanal	3700	10000	8000
3-Methylbutanal	1394	675	658
trans-Non-2-enal	3.14	15.0	15.0
Saturated aldehyde mixture (C4 to C10)	118	162	165
Unsaturated aldehyde mixture (tC4 to tC9)	33.6	21.0	22.0

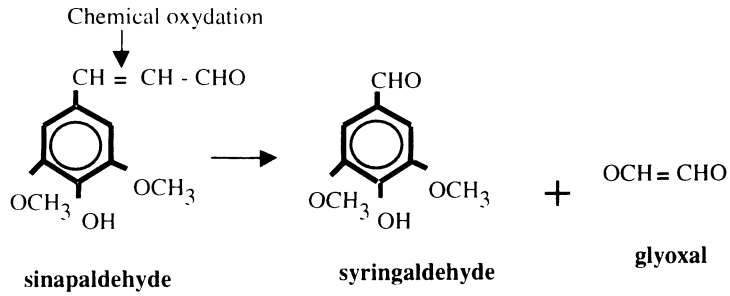


Figure 10–9 Chemical oxidation of an aromatic aldehyde leading to glyoxal.

more permeable to oxygen and yields more tannin. At this stage, oxidation is of prime importance, not only for the development of the substances originating from the wood but also for the distillate itself. Alcohol is oxidized into acetic acid, the quantity of which increases three-fold in 20 years; pH, which is 5 in a young wine-spirit, drops to 3.5; acids in turn become esters; and, in the end, only the higher alcohols remain relatively unchanged in relation to methanol.

According to Puech (1986), oak consists of 40–45 % cellulose, 20–25 % hemicellulose,

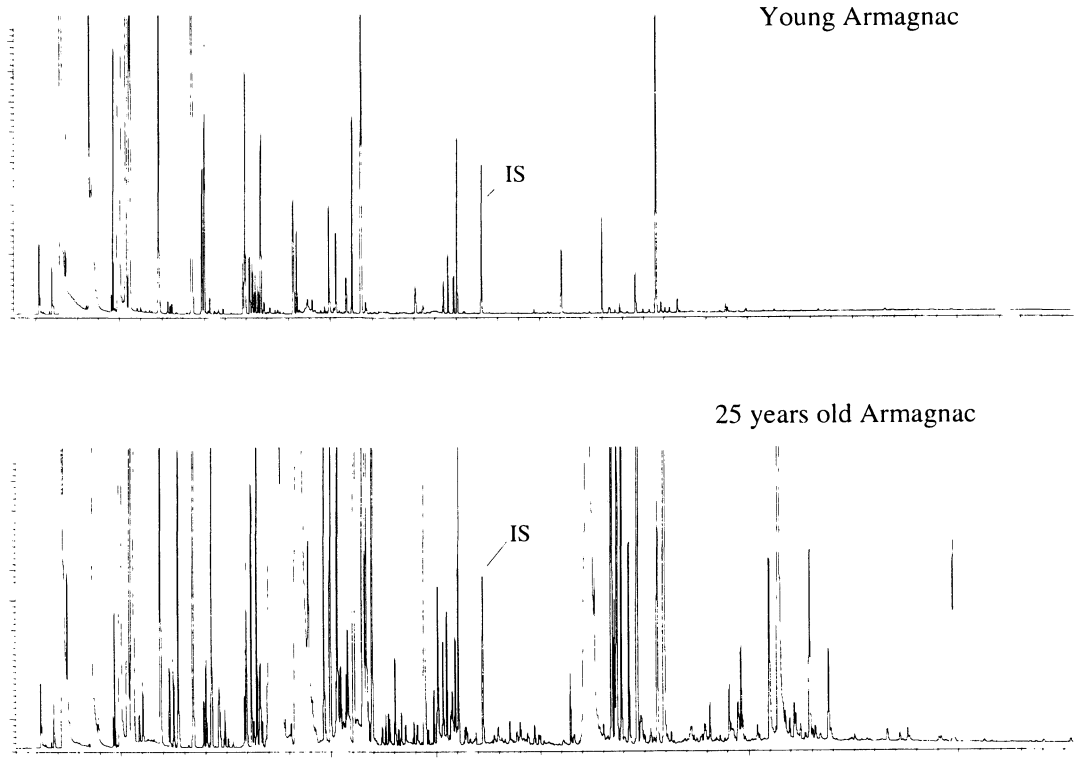


Figure 10–10 Gas chromatogram of PFBOA-derivative carbonyl compounds extracted from a new Armagnac spirit and a 25-year-old Armagnac. For chromatographic conditions see Figure 10–7.

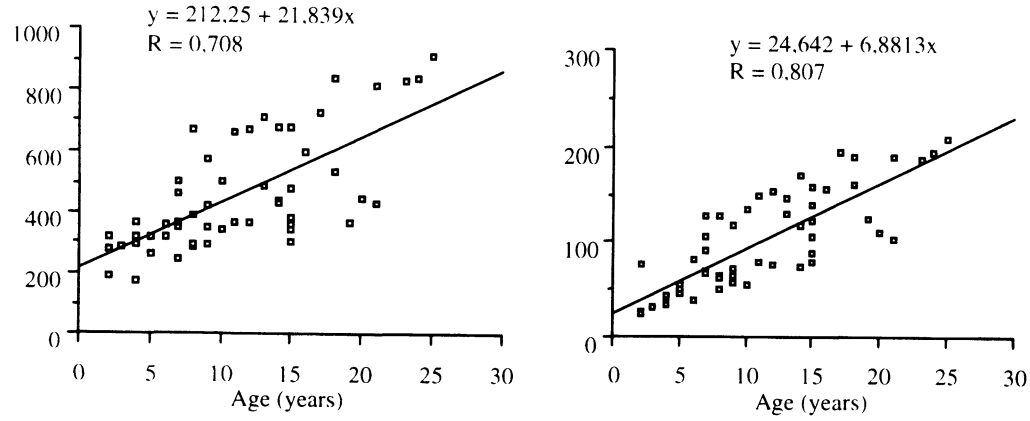


Figure 10–11 Amounts of 3-methylbutanal (left) and hexanal (right), two aging markers, in 54 Armagnac samples of different ages and origin.

25–30 % lignin and 8–15 % tannins. The optimal alcohol concentration to extract these components with wine-spirits is around 55 % vol. Armagnac just out of the still lends itself perfectly to harmonious aging.

The amount of substances extracted from the wood depends on whether the cask is new or old; over a 12-year period, a new cask can produce three times as much as an old one. Spirits with too much tannin (castalagin and vescalagin) can be harsh and astringent. With time, lignin contained in alcohol is transformed into aromatic aldehydes and phenolic acids. Armagnac contains vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde, but only the vanillin is detectable at tasting. Although there are a variety of aging methods, spirits are usually kept in new casks (400l) for 6 months to one year before being transferred to old casks.

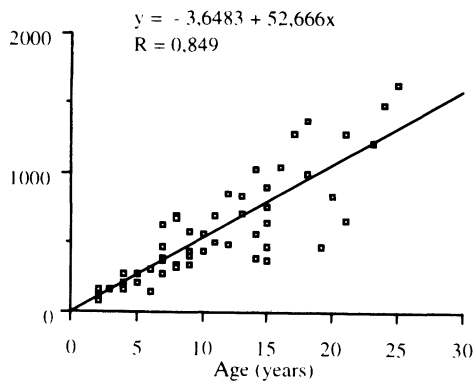


Figure 10–12 Glyoxal content in 54 Armagnac spirits from different origins as a function of aging.

Prior to being marketed, several wine-spirits are blended and the alcohol concentration of the blend ('the cut') is 'reduced' to a minimum of 40 % vol. with distilled water. The naturally golden yellow color can be enhanced with caramel. Sometimes, infusions or decoctions made from oak shavings are added to make the Armagnac more astringent, to give it more body; however, these preparations must be at least the same age as the youngest spirit used for the commercial designation of the final product (see below). Sugar solutions are sometimes added to attenuate the 'burn' of the alcohol (about 6 g/l).

Finally, before being bottled, the spirits are cold-processed (usually 1 week at − 5 °C) and passed through a cellulose filter to eliminate any possible cloudiness caused by an excess of calcium or fatty acids.

Vintage spirits from a single harvest of a particular year are sometimes sold with no prior 'reduction' of their natural alcohol concentration. Vintage Armagnacs constitute an exception among wine-spirits; some of them are extremely valued and fetch high prices.

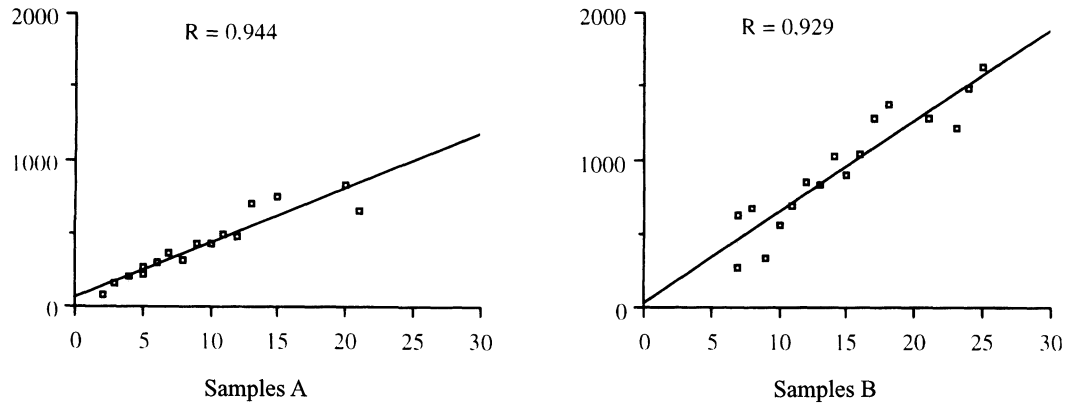


Figure 10–13 Amounts of glyoxal in spirits aged only in previously used oak casks (A), and in those aged for the first 5 years in new oak casks (B).

The various commercial designations (Table 10–7) are based on the youngest spirit in the blend ('cut'); the BNIA keeps updated registers listing the age (*compte d'âge*) and volume of all the different Armagnacs stored in any given storehouse.

WINE-SPIRITS

European legislation (EU Regulation No. 1576/89) distinguishes winespirits and brandy.

Regulations

Wine-spirits

According to regulations. wine-spirit is a spirituous drink with certain characteristics:

- It is obtained exclusively by distilling wine or 'winey' wine (vin viné) to 86 % vol., or by redistilling wine distillates to less than 86 % vol. (wine distillates are halfway between spirits and ethyl alcohol; mainly they must have retained the flavor and aroma of wine).
- It has a volatile substance content equal or superior to 125 g/hl 100 % vol. alcohol ('volatile substance' content incudes higher alcohols, esters, aldehydes, volatile acids and furfural).
- It has a maximum methanol content of 200 g/hl of 100 % vol. alcohol.

When aged, this beverage can continue to be marketed with the designation 'wine-spirits' if the period of aging is equal or superior to the period provided for brandy. This rule provides that general designations (20 different kinds of spirits) can be completed by geographical indications. The most famous French geographical designations are Cognac and Armagnac.

Table 10–7 Major commercial designations of AOC wine-spirits

Category	*Minimum age ('compte d'âge')*	*Average age*
'Three Stars'	2	About 2 years
V.O., V.S.O.P.	4	5 years
X.O., Extra, Napoleon, Vieille, Reserve, Hors d'Age	5	6 years

Brandy

Brandy is a spirituous drink with the following character:

- It is obtained from wine spirits blended or not with wine distillates distilled to less than 94.8 % vol., on condition that such distillates do not exceed 50 % proof maximum in the finished product.
- It is aged in oak containers for at least one year, or for a minimum period of 6 months if the capacity of the oak casks is less than 1000 litres.
- It has a volatile substances content (see section 9.1.5.1) equal or superior to 125 g/hl 100 % vol. alcohol resulting exclusively from the distillation or redistillation of the raw materials brought into play.
- It has a maximum methanol content of 200 g/hl of 100 % vol. alcohol.

Distillation

As a rule, brandies are distilled in columns containing several dozen plates. Old stills were entirely made of copper, but because the sulphur dioxide in the wine corrodes the stills and particularly the phlegm collector plates, copper has gradually given way to stainless steel; today, copper is used only for the topmost parts of the rectifier columns (for drawing the spirits).

Wine Rectifiers (Mariller, 1925)

For a long time, only phlegms were rectified, that is the distillery carried out two successive operations: (i) wine distillation and recovery of phelgms; and (ii) rectification of phlegms. With the advances made in the conception and building of distilling equipment, continuous rectifiers now exist which process the fermented wine, making it possible to obtain 96.5 % vol. rectified alcohol in a single operation. Wine rectifiers can be divided into three categories: indirect, direct and semidirect appliances.

Indirect Rectifiers

As indirect rectifier is illustrated in Figure 10–14. The term indirect means that rectification involves a traditional distillation process, except that phlegms are not cooled and sent into trays but go directly into the continuous rectifier appended to the column.

The distillation column (A) produces the phlegm which is then extracted while hot from the distillation column and sent directly to the purifier column (B) of the continuous phlegm rectifier. The purifier column extracts the head foreshots, after which the purified phlegm is sent to the rectifier column (C) from which the potable pasteurized alcohol is drawn off; the non-pasteurized alcohol, which is downgraded, and the low- and high-fusel oils are also extracted.

Guigon and Cogat (1991) proposed the addition of special devices to the columns to recycle the most volatile substances of organoleptic interest (Figure 10–15). This specific draw-off determines the final amount of tailings in the distillate. For the subsequent production of wine-spirits, only the higher alcohols are partially eliminated (high- and low-fusel oils) in order to recompose the distillate as desired. In this case, the resulting alcohol can only be called distillate and not 'spirits', because of the high percentage of alcohol—higher than 86 % vol.—required for sorting heavy impurities.

Methanol is extracted on a special multiple plate column (about 50 plates). This column has the disadvantage of eliminating not only the methanol but also volatile compounds of organoleptic interest; a small column can be appended which separates the methanol and the volatile substances, the latter being reintroduced into the distillate.

Batch Rectification for the Production of Wine-Spirits or Distillates (Figure 10–16).

This kind of still has a boiler similar to that of the Charente still or the cylindrical boiler stills. Primary spirits can be slightly oxidized before redistillation. This batch rectifier comprises a steam-producing device, a 30-plates column and cooler accessories and circuits. Head and tail products can be recycled in the boiler.

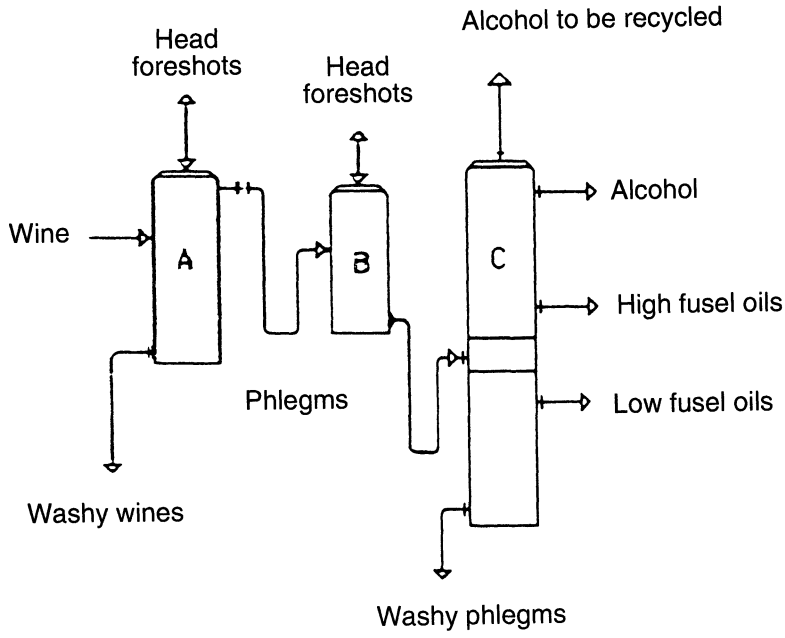


Figure 10–14 Indirect continuous wine rectifier (according to Mariller, 1925). A, distillation column; B, epuration column; C, rectification column.

Composition of Brandies

Because of the nature of the raw material brought into play (usually red wine) and the way they are produced, brandies contain far fewer volatile substances than AOC spirits (Armagnac, Table 10–1); higher alcohols are rectified by specific fusel-oil separation processes; and head products lose most of their ethyl acetate and esters during the ethanal and sulphur dioxide elimination process.

The making of brandy is usually a way to salvage defective wines or production surpluses. However, there are some good quality brandies made from wines specially grown for the purpose and vinified with limited quantities of sulphur dioxide.

Aging and Merchandising Preparations

As provided for by law, brandies are aged in wood containers (sous bois); different processing methods can be used; cold processing, ion-exchange resins to eliminate sulphur dioxide, calcium and copper cations; sugar, caramel and boisé (infusions from oak shavings) may be added. Brandies are reduced with deionized water and must have a 37.5 % vol. minimum alcohol concentration. Practically no wines have been distilled in France to make brandies since 1990. The entire production of French brandy is exported.

ETHYL CARBAMATE IN WINE SPIRITS

Ethyl carbamate (EC) in wine distills only in a small proportion. Riffkin *et al.* (1989) made a similar observation in other substrates. The urea in wine is not a precursor of the EC in brandies. Cantagrel *et al.* (1989) showed that plant pesticides present in wine before distillation (i.e. methyl carbamates, dithiocarbamates) did not change the final EC content. Thus, the EC con-

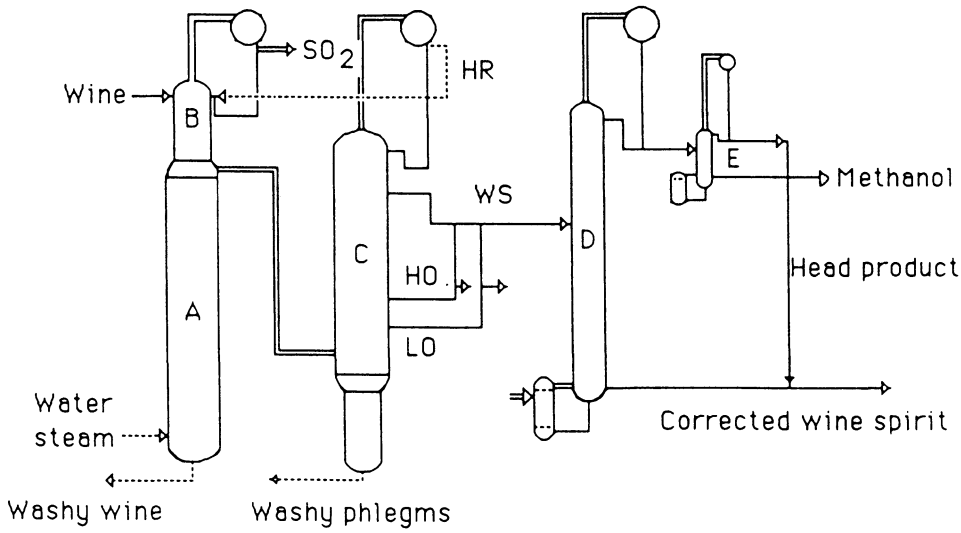


Figure 10–15 Continuous wine rectifier with head foreshot recovery (according to Guigon and Cogat, 1991). A, distillation column; B, desulphitation column; C, concentration column; D, demethanolation column; E, column for separating volatile esters (head products from methanol); HR, head products recycling; LO, low-fusel oils; HO, high-fusel oils; WS, wine spirit.

tent of brandies depends primarily on several precursors relating to the type of wine and the distillation process. These precursors are formed or released during distillation.

Role of the Distillation Process

Table 10–8 indicates the EC contents in parts of wines or distillates obtained with a two-stage pot still or a continuous still. Cold wine, wine in the wine heater, and the residual liquors (washy wine) of continuous distillation contain low quantities of EC. On the other hand, the levels are very high in all the fractions of continuous distillation. The presence of EC in the heads taken at the top of the wine-heater indicates that the precursor is very volatile. Since the wine is at a temperature lower than 85 °C, it cannot result from the volatilization of the EC in the wine. The heart is the richest part: the EC is not trapped in the tails since when this fraction is taken, the EC is not yet formed. The latter appears only during the hours following distillation, (Bertrand *et al.*, 1990) so it remains in the heart where it reacts with ethanol.

In the case of distillation by the two-stage process, a part of the EC is already present in the brouillis. This is eliminated in the tails, just like the EC of the "seconds" which, according to the distillation process, is either mixed with the wine or with the brouillis. In addition, in the case of Charente distillation (two-stage pot still), the copper of the boiler is cleaned at every loading of the pot still so a possible precursor could thus be trapped (Christoph *et al.*, 1988). In the case of the continuous still, a similar phenomenon is observed: during the hours following the cleaning of the distillation column, the rate of EC formation is very low, then it goes up gradually with time to stabilize approximately after 24 hours.

Copper metal seems to trap the precursor of EC in the liquid phase (wine) or even prevents the precursor when formed from releasing itself. However, according to Cook *et al.* (1990), the presence of copper ions increases the thermal stability of the cyanhydrin of isobutanal, a possible precursor of EC in grain distillate. A similar phenomenon could occur in the case of continuous wine distillation. The lack of copper ions due

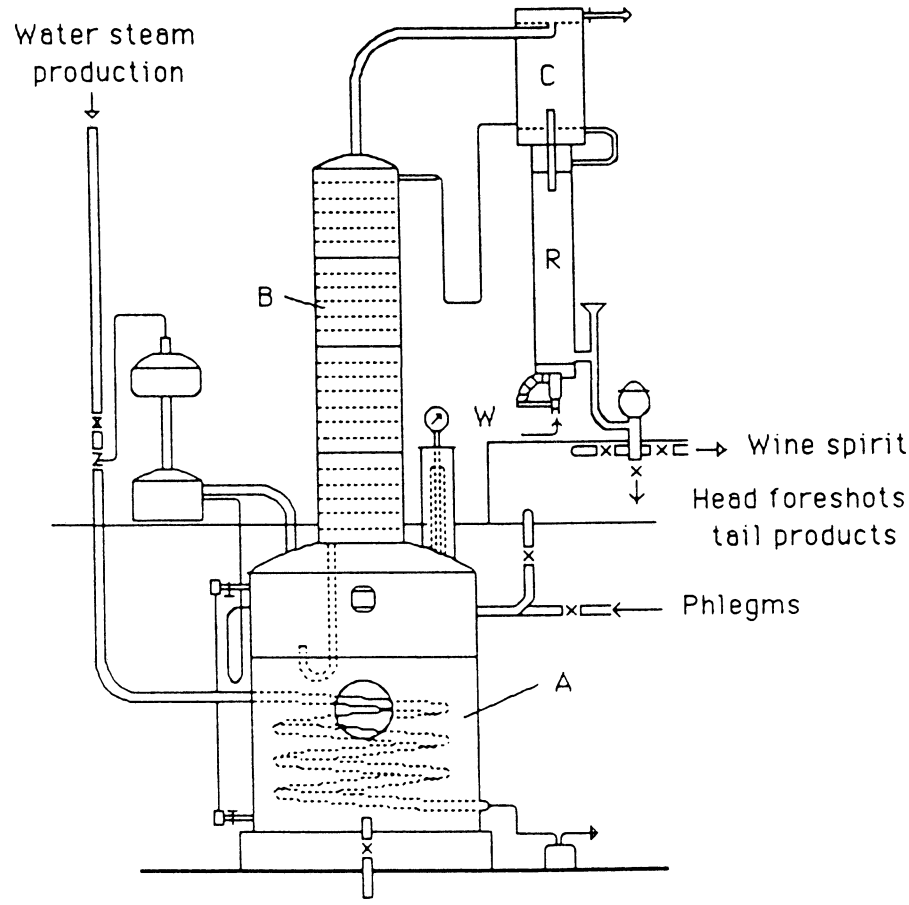


Figure 10–16 Batch rectification still for the production of wine spirits or distillates. A, boiler; B, distillation column (30 plates); C, condenser; R, refrigerator (cooler); W, water.

to the progressive clogging of the fractionation column does not make it possible to stabilize this intermediate compound. It should be noted that isobutanal is the principal aldehyde of wine brandies after ethanal (Vanderlinde and Bertrand, 1992).

Role of the Vine Cultivar

Among the different types of white wines generally used for distillation, spirits from 22 A Baco show considerably higher EC contents if obtained by continuous distillation (Table 10–9).

Table 10–8 Ethyl carbamate (µg/L) according to the distillation process

	Cold wine	Wine of the wine-heater	Washy wine	
	3	4	10	
Two-stage distillation	brouillis	heads	heart	seconds
	48	30	52	55
Continuous distillation	Heads	heart	tails	
	293	446	283	

Table 10–9 Ethyl carbamate in brandies obtained by continuous distillation, according to type of vine

Type of vine	*Ugni blanc*	*Folle blanche*	*22A Baco*	*Colombard*
Ethyl carbamate in spirit (µg/L)	183	145	392	185
Nitrogenous compound in the wine:				
Number of samples	5	3	9	—
Amino acids in must (mg/L)	809	1120	1460	—
Alanine (mg/L)	54	97	136	—
Ethylamine (mg/L)	0.58	0.63	2.04	—

A characteristic of 22 A Baco wine is its high content in amino acids, particularly alanine and ethylamine, of which the latter is formed from this amino acid during malolactic fermentation. Therefore, A Baco wine seems to have specific characteristics associated with the level of some nitrogenous compounds able to play the role of precursor in the formation of EC.

Search for a Precursor in the Case of 22 A Baco Wine

The use of a laboratory microstill (Bertsch *et al.*, 1990) made it possible to study the evolution of EC according to the presence of copper, and conservation according to light conditions (Baumann and Zimmerli, 1988; Riffkin *et al.*, 1989).

Catalytic Role of Copper

The EC content 12 hours after distillation is 300 µg/L in the presence of copper turning in the still. On the other hand, it is only 50 µg/L if this copper turning is removed. However with light and even without copper, the EC evolves quickly to reach the same value as in the presence of copper. Copper accelerates the reaction and its absence does not prevent it (Figure 10–17).

Role of Light

Like copper, light accelerates the reaction. With darkness, it is delayed, and it becomes very slow in the absence of copper. However, it does take place. To assay EC in wine brandies ready for consumption, it is not necessary to expose them to the light because no notable evolution has ever been observed.

Hydrocyanic Acid

In distillates, the most frequently reported precursor of EC is hydrocyanic acid. In the case of stone-fruit brandies, this presence is well-known (Adam and Postel, 1987; Laugel *et al.*, 1987). The amygdalyne of the kernels forms benzoic alde-

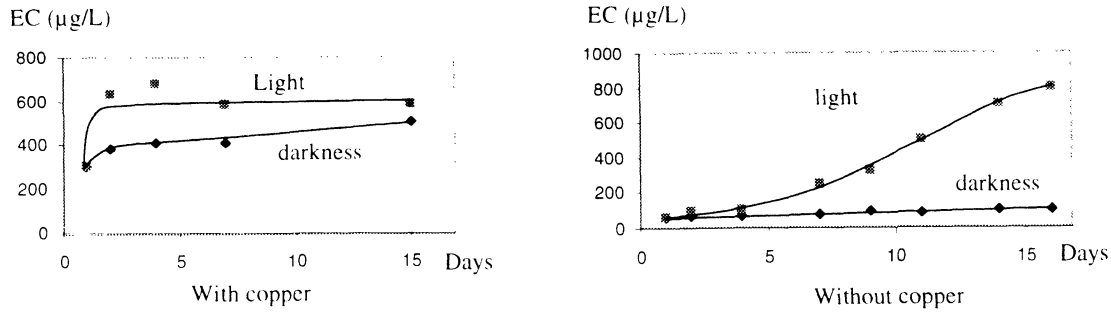


Figure 10–17 Evolution of EC content in a 22 A Baco wine distillate after distillation and exposure to light for 12 hours, then conservation either with light or in darkness.

hyde and hydrocyanic acid which gives part of their typicity to these spirits. Hydrocyanic acid is also cited in the case of grain alcohols (Cook *et al.*, 1987). In our laboratory Bertsch (1992) quantified the hydrocyanic acid according to the specific reaction of Lambert (according to Cook *et al.*, 1991). From a Baco wine distillate obtained using the microstill, he followed the evolution of hydrocyanic acid as well as the appearance of EC during conservation. The results suggest that hydrocyanic acid is one of the EC precursors in Baco wine brandies. The reactions described by Baumann and Zimmerli (1988) ranging from hydrocyanic acid to EC can take place since wine brandies contain all the carbonyl compounds necessary for the oxidation of hydrocyanic acid via peroxides; e.g. diacetyl, pentanedione, and methylglyoxal (Vanderlinde *et al.*, 1992).

Use of Ion Exchange Resins to Reduce EC Content

Study of the various technological parameters has shown that the two principal factors responsible for the formation of EC in certain wine brandies are, on the one hand, the Baco type of wine, and on the other, the use of the continuous still. It is neither possible nor perhaps desirable to remove these two causes of formation, at least in the short run. Anyway, Baco should have disappeared before the year 2010.

Neither the various treatments of musts, the clarification of wine, or early distillation appear to be really effective in eliminating EC. Nor do modification of the still or the methods of distillation (temperature adjustment by using only serpentines), or even changing the alcoholic strength of the distillate or pulling the heads and tails). The treatment of brandy itself by various processes (charcoal, resins, adsorbents) does not eliminate EC, either. On the other hand, the implementation of ion exchanging resins could be useful (Bertrand *et al.*, 1990 a,b). First, cupric ions have an influence on EC formation. Their elimination by a cation exchange resin could thus modify the final EC content in brandies. Second, two acids (hydrocyanic and isocyanic acid) are thought to be the mechanisms of EC formation. Fixing them with an anion exchange resin could thus lead to positive results.

Since promising positive results were obtained in the laboratory using brandies produced on a microstill functioning according to the principle of continuous distillation, tests were carried out in a distillery. A resin already used for more than 15 years for the treatment of wine brandies was tested. It was a strongly basic anion exchange resin for food (E 561). We passed 400 L of wine brandy on 2 L of resin for 19 hours. Analysis of samples enabled us to confirm the results obtained in the laboratory (Table 10–10). The EC content was decreased by more than 99 % in all samples taken during the experimentation.

A new food resin (IMAC HP441) used to purify drinking waters and approved by various public health authorities such as the Higher Council of Public Health (France), the Food and Drug Administration (United States of America)

Table 10–10 Treatment of a wine brandy with an anion exchange resin with respect to ethyl carbamate content (measurement made 7 days after distillation and exposure to daylight in white glass bottles)

Duration of resin use (hours)	*Ethyl carbamate in distillate (µg/L)*	
	Control	Treated
0	423	2
2	388	1
8	438	3
13	511	3
19	483	4

and the Bundesgesundheitsamt in Germany was activated by 5 cycles of successive passages of 2 bed volumes NaCl 1 M, 20 bed volumes of distilled water and sodium hydroxide 1 M, plus a final cycle with diluted acetic acid. A series of experiments was done with this resin on brandies running out of the continuous still.

The strong reduction in the EC content with the use of an anion exchange resin (Table 10–11) (642 µg/l for the control and 28 µg/L for treated brandy) indicates that the direct precursor is a negatively charged compound, most probably an acid. On the other hand, the elimination of copper with a cation exchange resin had no notable effect on the EC content in this experimentation. The passage of brandies on anion exchange resins at the outlet of the still makes it possible to lower the EC content by more than 80 % by fixing the precursor which is thus of acid nature. One volume of resin makes it possible to treat at least 8,000 volumes of brandy. In all cases, the EC content even after 6 months of conservation in the light was lower than 50 µg/l when the brandies were treated with the resin. If the resin used for the treatment is prepared suitably, it is only the EC content which changes and not the other components. There was no significant difference between control and treated brandies, either by chemical analysis or tasting.

In wine brandies, the precursors of the ethyl carbamate are not yet clearly identified. They are neither the natural ethyl carbamate of the wine nor a substance derived from pesticides, so they could be hydrocyanic acid or a very similar compound. Among the various types of vines studied, 22 A Baco gave brandies with a 2-fold higher EC content. Some nitrogenous compounds (alanine, ethylanine) in these wines occur at concentrations much higher than in other types of wines. The process of distillation using a two-stage pot still allows the elimination of the EC formed initially when obtaining the brouillis. The residual content in brandy is thus much lower than in the case of continuous distillation. In addition, in Charente distillation, the copper of the boiler is perfectly cleaned between each loading so less EC is formed than in the continuous process. In distillates, the formation of EC starting from the precursors is catalyzed by copper ions and light. If necessary, the EC content can be reduced by eliminating the acid precursor(s) with an anion exchange resin directly placed at the outlet of the still. Generally speaking, the EC content in wine brandies is low and meets the requirements of current legislation.

Table 10–11 Role of resin type on reduction of ethyl cabamate

	Ethyl carbamate (µg/L)	
	Control	*Treated*
Anion exchange resin	642	28
Cation exchange resin	438	400

CONCLUSION

Wine spirits of viticultural origin belong to the French cultural heritage; they also constitute a major market of our economy. Furthering our knowledge of their composition reveals that traditional wine-spirits have exactly the same composition as wine; only the heaviest and most polar products are rectified (acetic acids, phenyl ethanol, polyols, etc.). Major defects can only be eliminated with the distillation column, but at the cost of eliminating components contributing to quality. Good quality wine-spirits can be made only with good quality wines; expensive aging in oak casks should be reserved for noble products.

ACKNOWLEDGEMENTS

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11

Whiskies

J.R. Piggott and J.M. Conner

INTRODUCTION

Scotch whisky is the best-selling spirit drink in the world, with Scotch, North American, and other whiskies taking 17 %, 12 %, and 6 %, respectively, of the market in 1993 (International Drinks Bulletin, 1994). Whiskies are distilled alcoholic beverages, prepared from cereals fermented with yeast and normally matured in oak barrels. There are many possible ways of producing whiskies, within the limitations set by the materials and processes available, and details vary depending on custom and regulation in producing countries. The products now available are those that have evolved under local circumstances, and subsequently have been stabilized by legislation. The European Union (EU) definition of whisky (EEC, 1989) is fairly broad, and defines the starting material (any cereals), starch degrading enzymes, fermentation, distillation at < 94.8 % v/v (so that the flavor is derived from the materials used), maturation in wooden casks of less than 700 l for at least 3 years, and offered for sale at a minimum 40 % v/v. The United Kingdom (UK) definition of Scotch whisky is broadly similar, and can be traced back to the original Royal Commission definition of 1909 (see, e.g., Daiches, 1978), which offered the first formal definition of whisky. Among other findings, it permitted the use of cereals other than the traditional malted barley. The current definition is essentially the same (SI, 1990), and differs from the EU definition only in that the process must be carried out in Scotland, the enzymes must be derived from malt, and additives other than caramel are explicitly excluded.

The other major whisky-producing areas have their own sets of regulations. The basic definition of whisky in the United States (USA; Bureau of Alcohol, Tobacco Products and Firearms, 1985) specifies a cereal distillate of less than 190 °US Proof (95 % v/v), retaining the flavor characteristics generally attributed to whisky. Within this definition many types of whisky are closely specified, by control of cereals, strength of distillation, and maturation period, strength, and container. A wide variety of blends is catered for in terms of the designations to be used in labeling (Booth *et al.*, 1989).

In contrast, Canadian regulations are relatively unrestrictive, and have more in common with the EU approach. USA and Canadian regulations also permit the use of "blending materials" (sherries, blending wines, and other spirits) at various

levels (Booth *et al.*, 1989). Japanese regulations specify three classes of blended whiskies, depending on the grain whisky content, which receive different taxation treatment. Grain whisky in this context means whisky from any grain, including malted barley. As a result many Japanese blends contain a proportion of imported malt whisky (Booth *et al.*, 1989; Watson, 1993).

EU and USA regulations also include provision for grain spirits or grain brandies that are essentially similar to whiskies but not matured. In other parts of Europe (e.g., Poland), similar spirits are produced that are essentially vodkas, matured briefly and flavored with wood extracts or other materials, and that may or may not meet regulations commonly accepted for whiskies.

MATERIALS

Corn (maize), rye, barley, and wheat are the major cereals used for whisky (Bronsky & Schumann, 1989). These grains have traditionally been the major sources of starch for whisky production, and meet the main criterion of a high starch content (Table 11–1), to permit the greatest yield of spirit. Within this initial selection, other characteristics can be specified for optimization of quality and yield.

Corn (*Zea mays*) is most used for whisky production in the USA, and was the prime cereal used for Scotch grain whisky. In Scotland, however, it has been largely displaced by European wheat, owing to the price effects of EU agricultural policies (Brown, 1990). USA production of corn accounts for over 40 % of total world production, whereas EU production is less than 5 % of the total. USA distillers use primarily dent corn (*Zea mays indentato*).

Rye (*Secale montanum*) is a minor crop in the USA and Canada, major production being in Eastern Europe and states of the former Union of Soviet Socialist Republics (Confederation of Independent States, CIS), and is used for its flavor contribution in whiskies, since it contains less starch than corn and wheat. Rye malt is also occasionally used.

Barley (*Hordeum polystichum*) is used primarily in the form of malt, for the flavor characteristics it provides in the spirit. In this case, the enzyme content (especially for mixed grain whiskies) is a major quality criterion, irrespective of the starch content, which is rather low. For distilling, barley varieties are selected on the basis of diastatic power (DP, largely a measure of

Table 11–1 Composition of the major cereals used for production of whiskies

	Composition (% of total)			
	Corn	*Rye*	*Barley*	*Wheat*
Endosperm	82	87	84	85
Germ	12	3	3	3
Bran	6	10	13	12
Chemical composition (dry basis)				
Nitrogen-free extract	69.2	70.9	66.6	69.9
Startch	72	68	63–65	69
Sugars	2.6	0	2–3	0
Protein	8	12.6	12	13.2
Soluble N % of total	4.7	0	11	0
Crude fiber	2	2.4	5.4	2.6
Fat	3.9	1.7	1.9	1.9
Ash	1.2	1.1	2	1.9

From Bronsky & Schumann, 1989.

ß-amylase), α-amylase and fermentable extract (Bathgate & Cook, 1989). The EU is the main producer, along with the CIS, and it forms a relatively minor crop elsewhere. Scotch whisky is unusual in that the malt used for malt whiskies may be flavored with peat smoke, a practice originating in the use of peat as the primary fuel to dry the malt. Malts are normally classified on the basis of the content of phenols, up to 50 ppm (Bathgate & Taylor, 1977), but it is uncertain which compounds are responsible for the flavoring effects of peat smoke (Howie & Swan, 1984) though the peaty characteristic can be predicted from the phenol content (Withers *et al.*, 1996). Some nitrogen compounds have been proposed, and it was observed that groups of whiskies could be distinguished based on the relative levels of pyrazines and pyridines (Piggott *et al.*, 1993b). A high ratio was associated with Islay Scotch malt whiskies (typically heavily peated), and a lower ratio with Scotch Speyside malts and bourbon whiskies. It is unlikely that pyridines are directly involved in flavor, however, since they are not volatile at the pH of matured whisky (Delahunty *et al.*, 1993) except perhaps in the mouth (Chapter 4). Nitrosamine contamination of malt has been a recent problem in Scotch whisky (Nicol, 1990), arising from the use of natural gas in directly fired kilns (Bathgate & Cook, 1989). This can be controlled by the use of burners designed to reduce the production of nitrogen oxides, by burning sulfur to add SO_2 to the drying air stream, or by indirect firing. Cultivars are normally selected on the basis of extract and fermentability, corresponding to spirit yield (Swanston *et al.*, 2000), or enzyme activity in the case of malt for grain distilling. Enzyme activity should be considered under process conditions, as this will not be the same as activity measured under optimum laboratory conditions (Sim & Berry, 1996).

Ethyl carbamate is an undesirable trace component in distilled beverages, and action has been required to reduce its level (Nicol, 1990). It is formed by the ethanolysis, in the presence of copper, of oxidized volatile nitriles (Riffkin *et al.*, 1990), which arise from the cyanogenic precursor in malt (Cook *et al.*, 1990). It may also arise from the decomposition of dichloramino acids formed from the reaction of sodium hypochlorite with amino acids (Riffkin *et al.*, 1989a, 1989b). Ethyl carbamate levels should be kept under control by avoidance of sodium hypochlorite where possible and careful distillation of wash and low wines (Riffkin *et al.*, 1990); it may also be helpful to choose barley varieties and malting regimes to reduce the formation of hydrogen cyanide (Cook, 1990). Barley cultivars that do not contain the precursor, epi-heterodendrin, are being developed (Swanston, 1999; Swanston *et al.*, 1999).

Wheat (*Triticum vulgare*) is a major EU, USA, and CIS crop, with total production approximately equal to that of maize. As mentioned, it is used in some USA whiskies, and has largely replaced maize in the production of Scotch grain whisky. In this context the yield and price are balanced to give the best economics, and flavor or other characteristics are secondary.

MILLING, COOKING, AND MASHING

Mashing is the process of forming a fermentable extract. Two major routes may be followed, depending on whether a malted or unmalted cereal is used. In the former case, the process is essentially similar to the production of wort for beer brewing, with a clear or filtered extract being required to prevent "burning" in batch (pot) stills. In the latter case, in modern continuous processes in preparation for continuous column distillation, the separation stage has become redundant and the fermentation (and distillation) are commonly carried out with the total grain solids present.

Malt Whisky

In the case of batch mashing (most commonly in small distilleries typical of the Scotch industry), the initial step is a coarse milling of the

grain. It is important that malt has been well-modified when legislation does not permit the use of exogenous enzymes (e.g., Scotch whisky), and the objective of milling is then to obtain maximum extraction of fermentable sugars. Milling that is too coarse will cause loss of extract, and milling that is too fine, filtration problems.

A conventional malt distillery mashing process involves a multi-stage extraction of the malt (Wilkin, 1989). A batch of malt is loaded into the mash-tun, followed by the first water (4–4.5 metric tons per metric ton malt) at 64–68 °C. This is drained and a second water at a slightly higher temperature is added (1.5–2 metric tons per metric ton of malt). This is followed by a third and possibly a fourth water at a higher temperature, up to 95 °C, the quantity adjusted to give the intended starting specific gravity for fermentation. Alternatively, later extracts may be stored for recycle into the next mash. The temperature of the first water especially must be controlled to minimize enzyme damage; a proportion of the conversion of starch occurs during and after mashing, in the fermenter, and so temperature must be limited. This "secondary conversion" is obviously inhibited by destruction of residual malt enzymes, particularly α-amylase. The time required for this process is typically 8–12 hours, and in an effort to reduce these cycle times, many distilleries use lauter tuns. In order to achieve the faster drainage rates required, a lauter tun uses a shallower bed and careful design of rakes to stir the bed. Other systems may also be used, all aimed at producing a clear wort, with maximum extract recovery in the minimum time (Wilkin, 1983, 1989). Milling becomes more critical as filtration speeds increase, and generally a higher degree of milling is required.

Grain Whisky

A substantially different process is required for preparation of a fermentable wort from unmalted cereals. The batch process, traditionally used in Scotch grain distilleries, is straightforward and can apply equally to maize or wheat (Figure 11–1). The grain may be milled or whole; the cost of milling must be set against the energy saving, achieved by quicker cooking of the milled grain. The grain is loaded into batch pressure cookers with water (2.5 metric tons per metric ton grain) and steam injected to raise the pressure typically to 200 kPa for 2 hours (Wilkin, 1989). The cooked cereal is then transferred to the mash tun, and cooled to 62.5 °C, and ground malt is added to achieve the necessary conversion of starch. The malt may be dried, or may be used as "green" malt, thus saving the energy cost of drying. The most important characteristic of the malt is that it have a high enzyme activity, in order to minimize the quantity required, typically 10–15 % dry weight.

In a continuous process (Figure 11–2), the milled cereal slurry is mixed with a pre-malt (a proportion of the malt to be used for conversion), and preheated. At this stage some conversion occurs, and the viscosity of the mix is reduced to ease future processing. The main cooking stage is next, at about 165 °C, followed by cooling to 60 °C, addition of malt, and conversion. The wort is finally cooled again for transfer to the fermentation stage.

The Scotch whisky industry developed using maize as the main non-barley cereal, and the change to the use of wheat (Palmer, 1985) introduced some problems, requiring the removal of pentosans, small starch granules, and proteins (Forrest *et al.*, 1985). The total economics of the process may then be affected by the income obtained from the disposal of gluten.

The energy demand of the high-temperature cooking stage has prompted investigation of "cold cook" processes (e.g., Macher, 1982), but such methods require fine grinding of the cereal grain, and thus some of the energy saved must be set against that required for grinding.

FERMENTATION

The fermentation stage is similar to that of many other alcoholic beverages, and in most regulations yeast (*Saccharomyces cerevisiae*) is specified as the only organism. While malt and

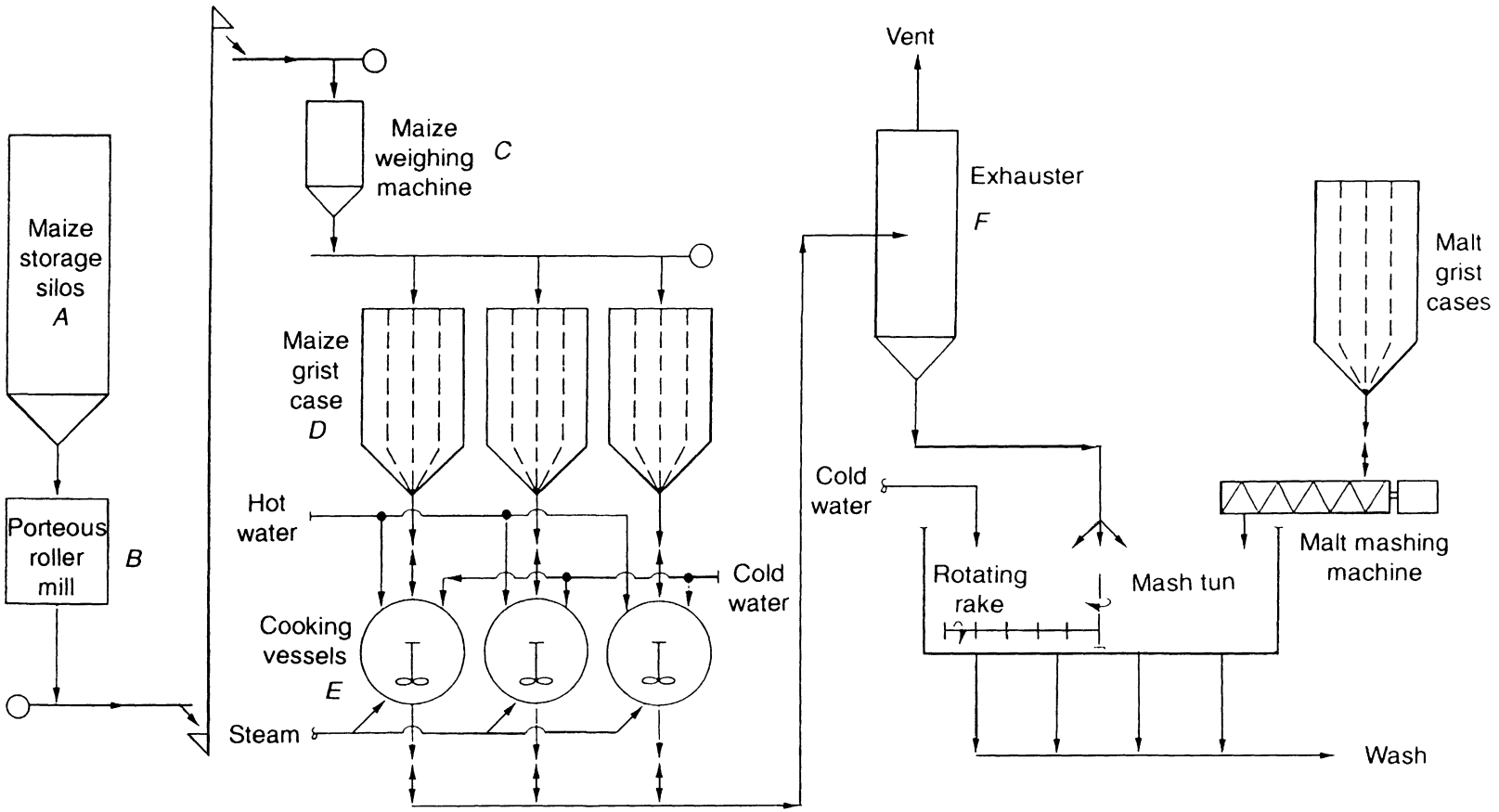


Figure 11–1 Cereal batch cooking equipment for Scotch whisky (Wilkin, 1989)

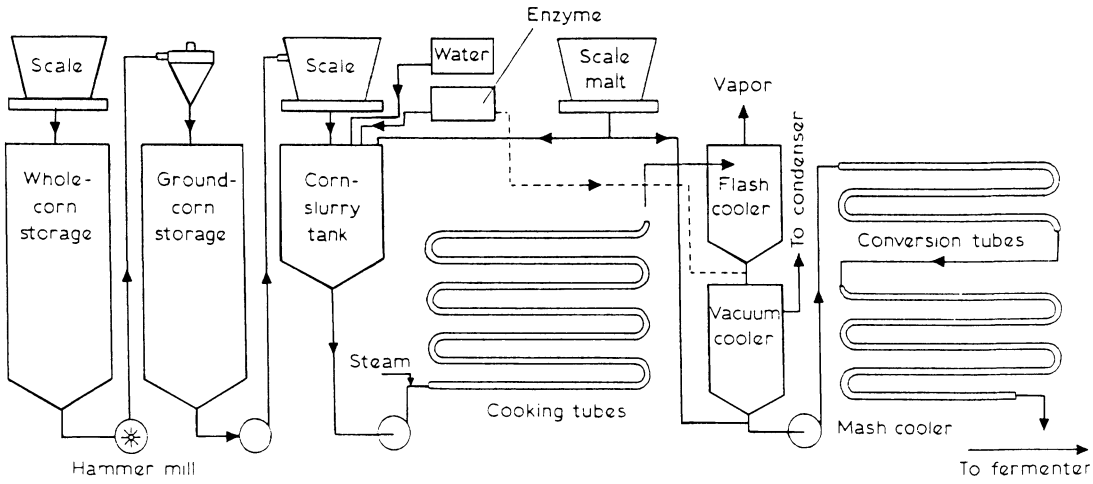


Figure 11–2 Continuous maize process for whisky (Simpson, 1985)

other cereals may be contaminated with a wide variety of organisms (yeasts and bacteria), whisky fermentations are started by pitching the wort with a known yeast culture, normally a specific strain of high-performance distilling yeast (Watson, 1981, 1984). Yeast specifications are shown by Korhola *et al.* (1989). To a limited extent strains may be selected to provide the required composition and flavor characteristics in the distillate, particularly the ester content (Lyness *et al.*, 1997). Yeast cultivation and storage conditions also affect its performance (Morimura *et al.*, 1998). In some cases, typically in Scotch malt production, a brewer's yeast may be used also because it is believed to produce a distillate of more desirable flavor (Korhola *et al.*, 1989). In principle, yields can also be improved by the use of yeasts expressing glucoamylase (Klaassen *et al.*, 1996).

In small-scale production, fermenters are closed vessels of traditionally wooden construction, with no means of temperature control. It is uneconomic to collect carbon dioxide, so it is simply vented. In larger scale production (e.g., in continuous grain distilleries) the fermenters are stainless steel, with facilities for cooling, and in some cases the ability to collect carbon dioxide. A typical fermentation will run for 40–48 hours, a very much shorter time than has traditionally been allowed. Shorter fermentations may be detrimental to spirit quality (Geddes, 1985), and excessively long fermentations allow considerable bacterial growth (Dolan, 1976, 1979) with the consequent loss of ethanol yield and danger of flavor defects (Makanjuola *et al.*, 1992; Barbour & Priest, 1988). Bacteria found have included *Lactobacillus*, *Leuconostoc,* and *Pediococcus* (Makanjuola & Springham, 1984; Priest & Pleasants, 1988).

DISTILLATION

Two distinct distillation systems have been used for production of whiskies; the batch or pot still, normally providing a double distillation (occasionally triple), to produce highly flavored spirit (Figure 11–3), and the continuous column still to produce lighter flavored spirits normally used as the base for blending.

Batch Distillation

Copper has traditionally been the chosen material for construction of batch stills, for ease of working, good heat conduction, and wear resistance. Polysulfides such as dimethyl disulfide and dimethyl trisulfide are important flavor con-

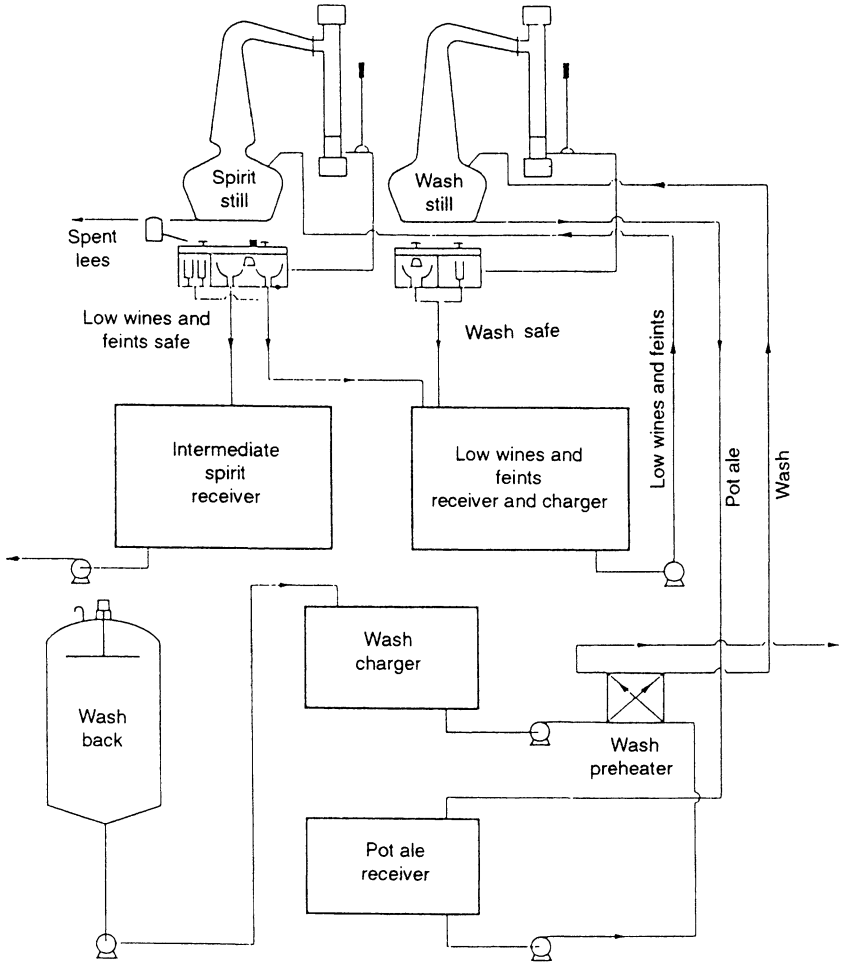


Figure 11–3 Typical malt distillery flow diagram (Nicol, 1989)

geners, possibly arising from methional in the wash (Prentice *et al.*, 1998), and more recently the importance of copper in influencing flavor, by aiding in the removal of sulfur compounds, has been appreciated (Chapter 15 in this volume; Whitby, 1992). A still consists of three major parts, the pot containing the liquid to be distilled, the swan neck and lyne arm, and the condenser (Figure11– 4). There are many minor variations on this basic pattern (Figure 11–5), which have largely unknown effects on the distillate. It is clear, however, that variations in the swan neck and lyne arm, by allowing differing extents of reflux, may affect flavor, and malt distillers are most reluctant to change the shape of a still when it must be replaced, to avoid unexpected effects. The pot may be heated directly by flame heating, or indirectly by steam coil or jacket. The first, wash, still may be fitted with a stirrer or rummager to prevent burning, in the case of directly heated stills (Nicol, 1989).

Wash typically contains about 8 % v/v ethanol, and efficient distillation should result in the collection of virtually all the ethanol, at about 21–23 % v/v, as low wines. The second, spirit, distillation proceeds in essentially the same way, except that a portion of the distillate (middle cut) must be selected as new spirit.

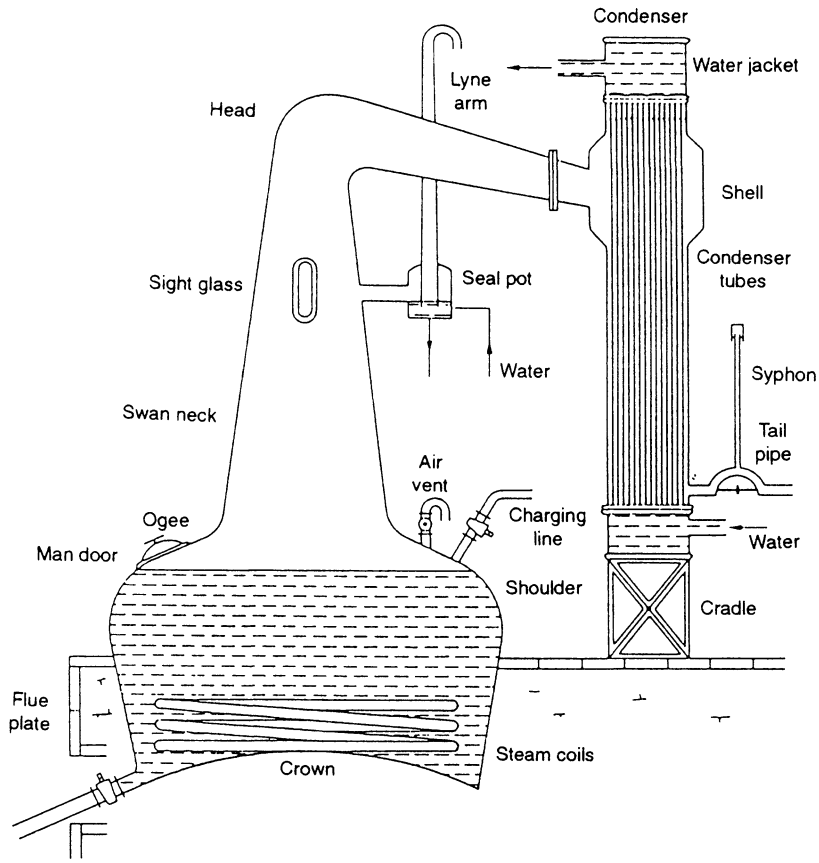


Figure 11–4 Plain wash still (Nicol, 1989)

Selection of the cut points, at the start and the end of spirit collection, is critical for the quality of the product, and depends on the particular distillery. After collection of spirit has ceased, distillation is continued until the ethanol is recovered, though it may be uneconomic to continue distillation to collect all ethanol. The initial and final fractions of the distillate, foreshots and feints, contain the undesirable highly volatile and less volatile congeners, together with a large amount of ethanol, and are recycled for redistillation with the low wines. The charge to the still is thus a mixture of foreshots, feints, and low wines, of 25–30 % v/v ethanol. The middle cut collected as spirit is typically 65–75 % v/v, depending on the distillery. The recycling of foreshots and feints into the distillation has substantial implications for spirit quality, and it is essential that a consistent and uniform procedure be followed, and that a consistent charge to the spirit still be maintained (Nicol, 1989; Whitby, 1992). The entire distillery system constitutes a complex balance, and if the balance is disturbed by changes in equipment or operating procedures, there may be undesirable effects on product quality.

Continuous Distillation

Column stills are used to produce the lighter grain spirits for blending (or occasionally for consumption as such). The continuous still was introduced to Scotch whisky production in 1827, and was subsequently developed by Aeneas Cof-

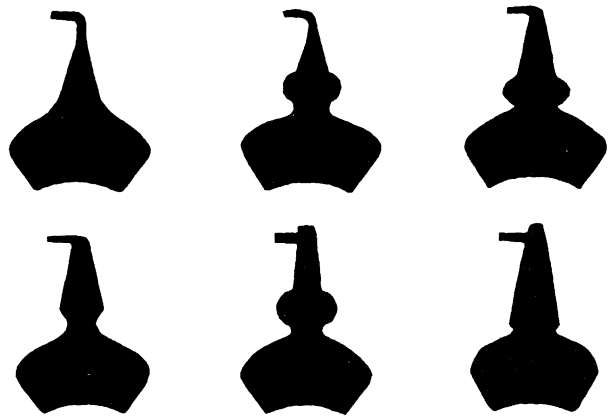


Figure 11–5 A selection of different pot still shapes (Whitby, 1992)

fey in 1830 (Moss & Hume, 1981). This type of apparatus is still known as the Coffey or patent still (Whitby, 1992). The still is constructed from two columns side-by-side (Figure 11–6), though functionally it can be regarded as a single column, mounted in sections to reduce overall height. The wash or beer is preheated by passing it through a tube winding through the second column (rectifier), and is then fed into the first column (analyzer) toward the top. Steam is sparged into the base of the column, and as the wash falls, the volatiles are stripped out and removed from the top of the column. The vapor then passes to the base of the rectifier, and the separation into alcohol and water occurs. The spirit product is removed at a level toward the top of the column. Fusel oil (largely *iso*-amyl alcohol) is taken off from near the base of the column, and foreshots (from the top) and feints (from the base) are recycled into the top of the analyzer.

A distillation column may be square, to facilitate the traditional wood and copper construction, but now is usually circular and more likely stainless steel (Whitby, 1992). Some copper must still be present in the system, however, and may be added as a "demister," a pad of copper mesh at the top of the analyzer (Panek & Boucher, 1989). Internally, the column consists of a series of plates with holes (originally simple "sieve" plates, but they may also be bubble-cap plates) to permit upward flow of vapor; the plates are linked by "downcomers," ending in weirs on the lower plate (Figure 11–7). The holes are sized to allow adequate vapor flow upwards, and in the case of the analyzer must be large enough to remain clear when cereal grains are in the wash (approximately 12 mm). The downcomers alternate from side to side across the column, so the descending liquid must flow across each plate, and be exposed to the vapor passing up through the holes. The weirs provide a liquid seal to prevent vapor from passing up through the downcomers.

North American practice for producing bourbon and other relatively highly-flavored grain spirits is to use a single distillation column, sometimes followed by a continuous pot distillation in a device called a doubler (Figure 11–8). The high wine (distillate) from the beer still is fed to the doubler at about 125 °US Proof (62.5 % v/v) and heated via steam coils, and the distillate is collected at 135–140 °US Proof (67.5–70 % v/v). The base effluent from the doubler is returned to the beer still (Panek & Boucher, 1989; Watson, 1993).

Multi-column systems are used for the production of less-strongly flavored spirits. The Coffey still produces grain spirit at about 94.5 % v/v, with a relatively strong flavor. The addition of further columns to the system facilitates the production of higher-purity spirit (at higher

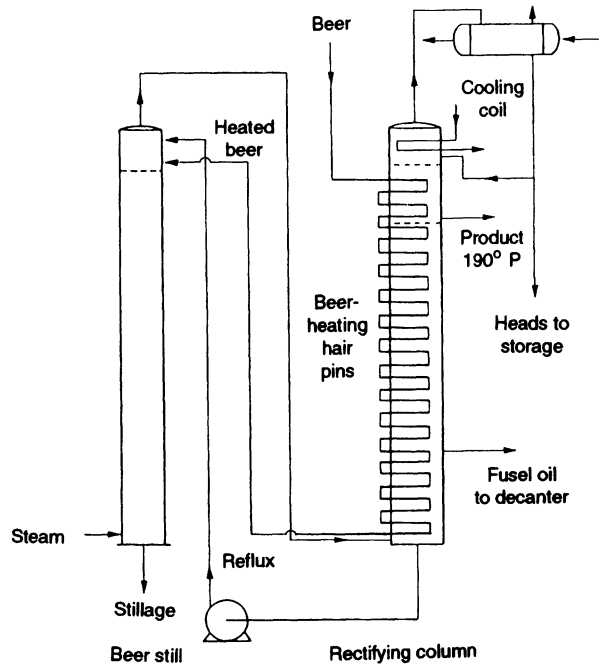


Figure 11–6 Coffey still (Panek and Boucher, 1989)

strength) in an economic way (Simpson, 1985), for use in distillation of gin, vodka, or other flavored products for which regulations simply call for the use of agricultural alcohol. A five-column still for neutral spirit production is shown in Figure 11–9, and Panek and Boucher (1989) described many variations of multi-column systems.

New distillates are commonly slightly reduced in strength prior to filling into oak casks for maturation. For Scotch, filling strengths range from 58 % to 70 % v/v ethanol, while in the USA "straight" whiskies are required to be matured at under 62.5 % v/v ethanol (Booth *et al.*, 1989). Filling strength can influence the quantity and composition of wood components extracted during maturation (Chapter 9; Baldwin & Andreasen, 1974).

By-Products

The two major byproducts of whisky production are the residues of the cereals used as the source of carbohydrate (spent grains), and the residues of the distillation (pot ale). These may arise separately, as in the case of Scotch malt whisky production, or they may arise together, as in the case of a whole-mash grain distillation. In either case they have some value as animal feed, and are normally dried as "dark grains." The economics of the process are finely balanced, and depend on cost of energy for drying, value as feed, and cost of alternative disposal (Alsaker, 1989). As mentioned above, carbon dioxide may be vented or collected and compressed. Other minor products include fusel oil from column distillations, for which there may be a market, spent lees from the second pot distillation, and the heads from column distillation. These are normally disposed of, and may require treatment on-site before disposal.

MATURATION

Maturation is an important step in the development of whisky flavor. Freshly distilled whis-

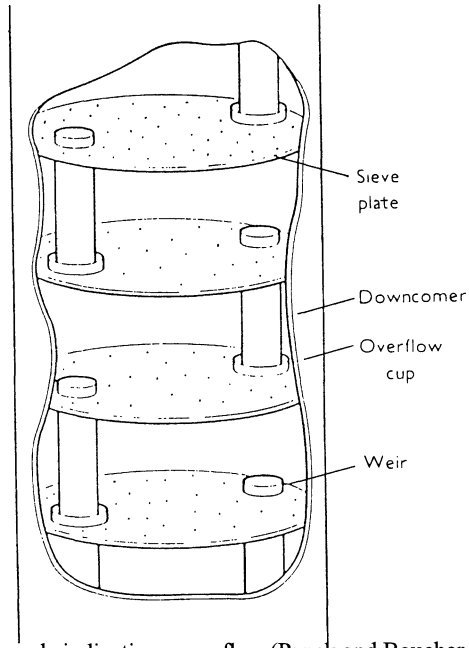


Figure 11–7 Typical column internals indicating cross-flow (Panek and Boucher, 1989)

kies generally have unacceptable sensory characteristics and are matured in oak casks to produce an acceptable product. During the maturation period the cask is more than just a physical container for the spirit, and the new distillate becomes highly modified as a result of its contact with wood. Though many reactions have been identified as occurring during maturation, there is no reliable chemical or physical index available for indicating the progress of maturation (Nishimura & Matsuyama, 1989). Consequently, the surest means of following the progress of maturation is by sensory assessment.

To gauge whether satisfactory maturation has occurred, the traditions and product expectations for the particular whisky have to be considered. While American bourbon and rye whiskies are matured in new charred oak casks, whiskies produced in Scotland, Ireland, and Canada are matured in oak casks previously used for the maturation of bourbon, or for the fermentation and shipment of sherry (Booth *et al.*, 1989). Consequently, while maturation of a Scotch malt whisky in a new charred oak cask may produce a well-matured whisky, it may not be readily identifiable as Scotch (Clyne *et al.*, 1993).

The legal minimum maturation time for most countries is 3 years, though where an age is stated on a bottle of whisky this is the minimum for all whiskies used in production, including grain whiskies used in blends. For certain types of American whisky a minimum of 2 years is specified.

Current Practice

Chemically, the distillery is the dominant factor in determining the concentrations of volatile compounds, while cask type is the dominant factor in determining the amounts of nonvolatile compounds present in the matured whisky. Few volatile compounds change significantly during maturation, and where this occurs such changes are frequently related to cask type (Philp, 1989). Color, pH, total solids, acids, esters, and sugars are very much influenced by cask type (Sharp, 1983). It is the combination of these constituents that produces the flavor and aroma of the final product. Casks are made from a limited range of

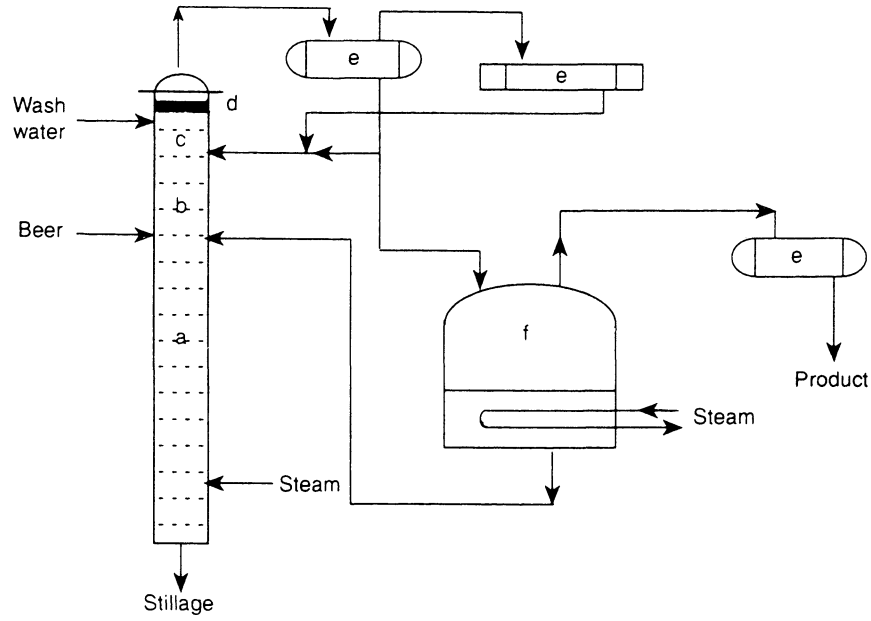


Figure 11–8 Schematic flow diagram of bourbon beer still and doubler: a) Beer still stripping section; b) Entrainment plate; c) Rectifying section; d) Copper demister; e) Condensers; f) Doubler (Watson, 1993)

oak species. Not only must the wood have the right structure to make a sound and viable container but it must also confer the right sensory properties on the maturing spirit. In practice whisky casks are made either of American white oak (*Quercus alba*) or European oak (*Quercus petraea* and *robur*).

Cask Type

In the USA there are strict regulations regarding maturation proof, aging period, and cask type. The standard maturation container is the American standard barrel (190 l capacity) made from kiln-dried American white oak. American white oak is a cooperage trade classification used in the USA for at least 10 botanical species, the principal being *Quercus alba* (Philp, 1989). New charred casks are required by law for the maturation of bourbon, rye, wheat, malt, and rye malt whiskies. Corn whisky, on the other hand, may be matured in new or used oak cooperage, but the new cooperage must not be charred. Light whisky, grain spirits, and grain neutral spirits are matured in previously used cooperage (Booth *et al.*, 1989).

There are two principal sources of casks for other whisky producers. The first type of cask includes all casks purchased, either directly or indirectly, from the Spanish sherry industry. These casks are mainly 500 l butts with smaller numbers of sherry hogsheads and puncheons. Sherry producers in Spain use both American and Spanish oak (predominantly *Quercus petraea* and *robur*). American oak is used for fino and amontillado sherries (Rickards, 1983), but Spanish oak is used for oloroso sherry. "Sherry" casks could therefore be a mixture of Spanish and American oak. Sherry casks are manufactured in Spain and shipped empty by arrangement with the distiller, who frequently specifies what type of cask (oak species and wine type) is desired, what the total contact time with maturing sherry should have been, and whether or not the cask should have been used for fermentation.

The second type of cask is hogsheads (254 l) and American standard barrels (191 l). Both are

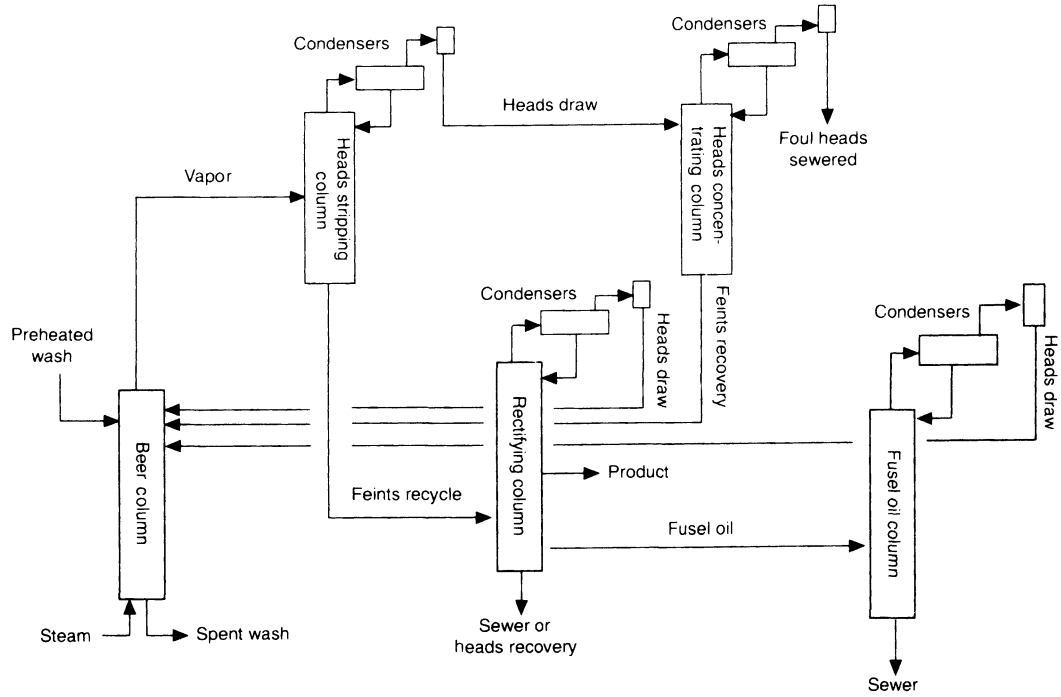


Figure 11–9 Five-column still for neutral spirit production (Wilkin et al., 1983)

made from staves that have had one fill (at least 4 years) with bourbon prior to first filling. American standard barrels would be received standing and used untreated. Capacity can also be increased to hogshead size by the introduction of additional staves and new oak ends.

There are marked differences in the sensory properties of spirit matured in the different cask types, and distillers will select one or another, or a mixture of both, to suit the different styles of whisky in their product range. Casks employed for the maturation of Scotch, Irish, and Canadian whiskies are used, repaired, and reused indefinitely until the cask is no longer a sound and viable container or, more commonly, until it has lost the ability to effect any sensory improvement over an economical maturation period. When this occurs, further fills can be obtained by recharring the inner surface of the cask. This process regenerates only some of the wood components found in new casks, and the spirit matured in these casks is significantly different from that matured in both new and refilled casks. Therefore, in a whisky warehouse the majority of casks will be refill casks, used an unknown number of times, with various degrees of repair work carried out on them and consequently with varying abilities to mature whisky. Normal practice is to average out these variables in the make-up of the final product by blending product of various ages and matured in different wood types (Philp, 1989).

Warehousing

Whisky was traditionally matured in stone-built, single-or multistory warehouses that were located beside the distillery. The bottom stories of these warehouses had cinder floors, with additional levels having wooden floors. Casks were stored in "stows" usually two or three high, sitting on top of one another with wooden runners between each layer. As production expanded, increased warehouse accommodation was required to store larger volumes of maturing spirit.

As a result, large centralized multistory warehouses were built. Basic construction was brick walls and insulated aluminium roofs. Steel racking with wooden runners was installed to allow casks to be stored up to 12 high depending on size. More recently some warehouses have dispensed with racking, and casks are stored on their ends on pallets, stacked up to 6 high, for easy access using forklift trucks. The environmental conditions were found to be very different in these large warehouses compared with a traditionally built warehouse. Sites closest to the roof are the driest and have the least stable temperature. Sites on the ground are the most stable in temperature and the wettest. Single-story sites tended to be relatively wet with unstable temperatures (Philp, 1989). During maturation the cask is not an impermeable container but, allows the evaporation of spirit (both ethanol and water) and an ingress of air (oxygen) during the course of maturation. The loss of a small percentage of spirit has long been an accepted part of maturation (called the angels' share), but this has been found to vary with the environmental conditions in a warehouse (Reid & Ward, 1994). Under controlled climatic conditions, temperature and humidity have been shown to affect the relative rates at which ethanol and water are lost. Raising temperature increased the evaporation losses of both ethanol and water. Humidity influenced the relative rate at which ethanol and water are lost: at high humidities more ethanol than water is lost and strength decreases; at low humidities more water than ethanol is lost and strength increases (Philp, 1989).

Evaporative losses during maturation show marked regional variations. In the USA, the relatively hot and dry climate encourages preferential loss of water vapor relative to ethanol, and consequently strength increases during maturation (Reazin, 1981). In Scotland the cool, humid environment favors the loss of ethanol over water and strength decreases during maturation. Indeed, very damp conditions were often created on the ground floor of sloping sites and were reputed to produce the best-quality whisky.

Under controlled conditions the nonvolatile content was significantly influenced by temperature, cask type, and to a lesser extent humidity (Philp, 1989). In multitiered warehouses in the USA, significant temperature differences between top, middle, and bottom tiers resulted in differences in the content of both volatile and nonvolatile components. In the warmest (top) tier, the physical and chemical reactions typical of maturation proceeded at a greater rate, but there was no optimal temperature for producing the desired product quality (Reazin, 1981).

Sensory Changes During Maturation

Maturation should produce a significant improvement in flavor quality. This results from the development of mellow or mature characteristics from the wood and a loss of the harsh or immature characteristics of the new distillate (Canaway, 1983; Reazin, 1983). Mature flavors that develop during maturation include vanilla, spicy, floral, woody, and smooth flavors. The harsh or immature characteristics have been described as sour, grassy, oily, and sulfury, though there is considerable variation in the vocabularies used (Canaway, 1983). Both the magnitude and the rate of change during maturation are dependent on the type of cask used (Piggott *et al.*, 1993a). Charring has been shown to increase the intensity of mature characteristics such as smooth, vanilla, and sweet and to decrease the intensity of immature characteristics (pungent, sour, and oily) (Clyne *et al.*, 1993). Cask reuse conversely decreases the intensity of mature characteristics and increases that of immature characteristics (Piggott *et al.*, 1993a).

Chemical Changes During Maturation

A number of chemical changes have been identified as important during maturation, and they may be categorized as the extraction of wood components, reactions involving distillate components, and solution changes that affect the release of aroma compounds.

Extraction of Wood Components

Many wood components are not present in a free state in the barrel wood and are the result of the decomposition of macromolecules forming the framework of the wood, such as lignin, cellulose, and hemicellulose. Polymeric material is also extracted from the wood, and this in turn may be broken down by the spirit solution (Nishimura *et al.*, 1983).

Oak consists of approximately 45 % w/w of cellulose, 15 % w/w of hemicellulose, 30 % w/w of lignin, and 10 % w/w of an extractable fraction consisting of volatile oils, volatile and non-volatile acids, sugars, steroids, tannic substances, pigments, and inorganic compounds (Nishimura & Matsuyama, 1989). The nature of the wood extract has a major effect during maturation, and its composition depends on the species of oak used, the pre-treatment of the oak wood prior to maturation, and the number of previous maturations.

The composition of wood extract is different for the different varieties of oak used for maturation. In general, European oaks yield higher concentrations of tannins and lower concentrations of oak lactones and scopoletin than American oaks (Guymon & Crowell, 1972; Puech & Moutounet, 1988), but this does not fully explain the sensory differences between whiskies matured in such casks. The compositional differences are due partly to the characteristics of different species of oak and partly to cooperage practices. In Europe stave blanks are commonly seasoned by air drying and casks are produced with only a light toast. In the USA stave blanks are commonly kiln-dried and casks are produced with a heavy char (Swan *et al.*, 1992).

Cask charring most common in the USA, as this process is an important contributor to the flavor of Bourbon whisky. Thermal degradation of the inner face of casks produces a layer of "active" carbon; greatly increases the yield of oak lactones and, colored and phenolic extracts (Reazin, 1981; Maga, 1989); results in the formation of maltol and 2-hydroxy-3-methyl- 2-cyclopentenone (Nishimura *et al.*, 1983) from wood polysaccharides; and degrades compounds such as *trans*-2-nonenal, *trans*-2-octenal, and 1-octen-3-one, which give resinous wood flavors (Chatonnet & Dubourdieu, 1998). Central to the increase in phenolic extract is the degradation of lignin to aromatic compounds such as vanillin, syringaldehyde, coniferaldehyde, and sinapaldehyde (Reazin, 1983; Nishimura *et al.*, 1983). During maturation these compounds are extracted by the spirit, and further breakdown of lignin occurs through oxidation and hydrolysis. Charred casks are generally used only once for the maturation of bourbon but are now commonly reused for the maturation of other whiskies. When they are repeatedly reused for maturation the yield of wood compounds extracted decreases (Reazin, 1981; Sharp, 1983). In tandem with this decrease in extract is a decrease in the development of mature characteristics, such as "smooth," "vanilla," and "sweet," and less suppression of immature characteristic such as "soapy," "oily," and "sulfury" (Piggott *et al.*, 1993a). Eventually a point is reached where the cask fails to produce any sensory improvement and is termed "exhausted" (Philp, 1989).

Another cask parameter that affects the course of maturation is the surface-to-volume ratio. Cask sizes range from the 558 l puncheon down to the 190 l American standard barrel. Smaller barrels have a higher surface-to-volume ratio, which results in quicker extraction of wood components but also in a higher rate of evaporation of ethanol and water. Given the same wood type and history, the smaller casks would be expected to produce a higher extract and to mature the whisky in a shorter period of time (Philp, 1989).

Reactions Involving Distillate Components

Changes in distillate character during maturation may be the result of the loss or suppression of aroma compounds. This may involve the evaporation of low boiling-point compounds through the wood of the cask, adsorption of compounds onto the surface of the cask, or chemical reaction that results in a less volatile product or one with different sensory characteristics.

Evaporation of volatile compounds through the cask surface occurs during the course of

maturation. For a model whisky the rate of evaporation ranged from 32 % of the total present in the spirit for acetaldehyde to 5 % for *iso-amyl* alcohols and 1 % for ethyl hexanoate and acetic acid (Hasuo & Yoshizawa, 1986). Evaporation is thought to be the main route for the loss of dimethylsulfide (Fujii *et al.*, 1992) and dihydro-2-methyl-3(2H)-thiophene (Nishimura & Matsuyama, 1989). The rate of evaporation may be affected by cask stave thickness, the air flow around the cask, humidity, and temperature.

Chemical reactions that alter distillate components include oxidation and acetal formation. Examples of oxidation include the formation of acetaldehyde and acetic acid from ethanol (Reazin, 1981) and the formation of dimethyl sulfoxide from dimethylsulfide (Fujii *et al.*, 1992). Oxidation in the maturing spirit is enhanced by the presence of wood extractives, particularly vicinal hydroxyphenols, which, with traces of copper from the still, are thought to act as a catalyst (Philp, 1986).

Acetal/aldehyde equilibria are established for most aldehydes and are important from an aroma standpoint, as aldehydes frequently have sour and pungent odors, while acetals are pleasant and fruity (Perry, 1989). The equilibrium between free aldehyde, hemi-acetal and acetal is affected by spirit pH and ethanol concentration (Perry, 1986) and so is partly influenced by cask type. Acetal formation is also important for removing acrolein, a potent lachrymator, from distilled spirits (Kahn *et al.*, 1969).

Reactions may also occur between wood components and components of the original distillate. Such reactions are typified by esterification, although they could theoretically include oxidation and acetal formation. During maturation the concentration of esters increases, due to the esterification of free acids by ethanol. A large part of this is due to the formation of ethyl acetate from acetic acid, either extracted from the cask wood or the product of ethanol oxidation (Reazin, 1981). Trans-esterification reactions are also thought to occur, which in the presence of the large excess of ethanol favors the formation of ethyl esters. Aromatic acids extracted from the cask wood such as syringic and vanillic acids are also known to form ethyl esters during maturation (Nishimura *et al.*, 1983).

Solution Changes That Affect the Release of Aroma-Compounds

Despite the range of reactions detailed above, the concentrations of many volatile compounds do not change significantly during maturation (Philp, 1989). Changes in pH during maturation, however, which may be cask dependent, affect the ionization state of weak bases, and consequently their volatility (Delahunty *et al.*, 1993). Decreases in pH had the greatest effect on pyridines due to their pKa (acid strength) values and greatly reduced their perception in the aroma of whisky.

Whiskies consist mostly of ethanol and water, with flavor-active components comprising only a very small proportion of the beverage. Recent research, however, has shown that ethanol and water do not form a homogeneous mixture over the whole compositional range (D'Angelo *et al.*, 1994). Only at low ethanol concentrations (< 17 %) is the ethanol evenly dispersed in water. At higher concentrations ethanol molecules cluster to reduce hydrophobic hydration so that the solution becomes a micro-emulsion. The aggregation of ethanol molecules increases the solubility of hydrophobic aroma compounds which in turn affects their release into the headspace of the spirit (Conner *et al.*, 1998).

It has been known for some years that wood maturation of spirits produces physico-chemical changes in the liquid detectable by differential scanning calorimetry (Nishimura *et al.*, 1983), small-angle light scattering (Aishima *et al.*, 1992), and mass spectrometric analysis of liquid clusters (Furusawa *et al.*, 1990). Such studies suggest a greater degree of nonuniform structure and an increase in large ethanol polymer hydrates in wood-matured spirits. Wood extracts have been shown to affect the aggregation of ethanol molecules, increasing the solubility of aroma compounds and consequently reducing their release into the headspace of the spirit (Conner *et*

al., 1999). These changes are consistent with the presence of either more, or larger ethanol aggregates in the mature spirit, with a greater capacity for solubilizing aroma compounds. These effects occur at both ambient and human mouth temperatures and so would alter the release of aroma-active molecules when spirit is both nosed and consumed. Wood maturation therefore will alter the release of certain distillate components in the glass and mouth, changing the aroma and taste of the matured spirit.

BLENDING

The aim of blending is to produce a consistent product that has a distinctive flavor (Lang, 1983). Generally blends consist of a light-bodied spirit mixed with a number of heavier-bodied spirits in a wide range of proportions. "Light-bodied" spirits are those distilled to high ethanol concentrations using continuous column stills and include Scotch grain whisky and American light whiskies, grain spirits, and grain neutral spirits. "Heavier-bodied" whiskies are either batch still products or column still products distilled to lower ethanol concentrations (Booth *et al.*, 1989).

The nature and components of blends are determined by the traditions and regulations of the country of origin. The actual process of blending, however, is very similar. Approved whiskies are delivered to the blending house and drained from the casks, in correct proportions, into passivated steel troughs. The troughs convey the whiskies to a blending vat where they are thoroughly mixed with mechanical agitators and compressed air. When the blend is correct, de-proofing water is added to the blend to reduce the strength for bottling. Minor variations do occur. In Scotland blending may be followed by a further period of maturation, and in Canada, distillates may be mixed prior to any maturation (pre-blending).

For Scotch whisky the light-bodied spirits are the products of up to 10 grain distilleries, situated mainly in the central belt of the country. The heavier-bodied spirits are the products of up to 100 malt distilleries, mostly in the Highlands and islands. Blends tend to be 60 % to 70 % grain whisky with as many as 50 malt whiskies. Recipes are often complex to prevent variation in quality or unavailability of a single whisky from having a noticeable effect on the quality of the blend. The complexity of blends is maintained by purchasing or exchanging new whiskies, which are matured in the producer's warehouses and delivered when they have been matured to the level required by the blender.

In the USA, where there are fewer distilleries and trading between competitors is uncommon, the components of a blend tend to be produced at only a limited number of distilleries. To increase the variety of components available to blenders, different cereals, fermentation conditions, distillation parameters, and maturation periods and cooperage may be used. Heavier-bodied spirits include bourbon, rye, wheat, malt, rye malt, and corn whiskies, while the lighter-bodied spirits are light whiskies or grain spirits and grain neutral spirits. The addition of blenders, up to 2.5 % by volume, is allowed, and these may include sherries and blending wines.

Irish, Japanese, and Canadian blenders have the same problems as blenders in the USA, in that they have a limited number of distilleries from which to chose. Again, variations in mash cereals, fermentation conditions, distillation parameters, and maturation time and cooperage are used to increase the variety of flavors available to the blenders. In Canada blended whisky may contain as much as 9.09 % flavoring on a liters of absolute alcohol basis, although this level is not usually achieved in practice. In Japan blends frequently include imported malt whiskies to give more flexibility in the formulation of blends.

FILTRATION

Most whisky is filtered prior to bottling to reduce the risk of haze formation. Spirits are traditionally matured at 50 % to 70 % alcohol by

volume but are bottled at 40 % to 45 % alcohol by volume. For heavier-bodied older whiskies and whiskies matured at higher strengths, this can result in a haze formation due to the fact that high-molecular-weight lipids and esters and ethanol-soluble lignins are less soluble in water than in ethanol. This problem is controlled by chill filtration, in which the whisky is cooled to between −10 °C and 10 °C and is held for a specified period of time before the problem compounds are removed by physical separation and adsorption by a filter (Booth *et al.*, 1989).

For Scotch whisky, long-term stability has been related to the total levels of ethyl laurate, palmitate, and palmitoleate at bottling strength. In blended whiskies the total level of these esters lies in the range of 12 to 18 mg/l, which carries a very slight risk of mild precipitation in extremely adverse conditions. Lower concentrations offer almost complete protection in all commercial situations, while higher concentrations will increase the risk of chill haze formation (Clutton & Simpson, 1992). Chill filtration of a malt whisky at temperatures of +2 °C and −2 °C produced significant decreases in the solution concentration of medium- and long-chain ethyl esters, alcohols, and acids. However, headspace analysis did not show any significant differences due to filtration. The medium- and long-chain components are all more soluble in ethanol than in water, and form saturated solutions when distillates are diluted. Chill filtration removes this excess from spirit without affecting the headspace (Piggott *et al.*, 1996). Under more severe conditions flavor changes can occur through the entrained loss of flavor compounds with the chill haze constituents or changes in flavor release due to the complete removal of long-chain esters. Consequently, process conditions must be chosen to balance haze stability and flavor effects.

The filter conventionally used is a plate and frame variety with preformed pads made of cellulose, or cellulose impregnated or pre-coated with diatomaceous earth. Typical particle-size retentions are on the order of 5 to 7 μm. Operational parameters depend on the batch size, the nature of the product, and the filtration rate required. In general, higher filling strengths and new wood require more filter area per unit volume.

RAW MATERIAL AND PRODUCT ANALYSES

The primary measurements of quality in whisky are aroma, taste, and visual appearance. To maintain the maximum yield and quality of the product, adequate analyses of raw materials and production processes are required to ensure that they meet the desired specifications.

Sensory Assessment

Whisky has traditionally been assessed by expert blenders with many years of experience and training within the industry. An experienced blender knows what flavors of distillate a still can produce, which are desirable, and how a whisky is likely to develop during maturation. The blender's task is then to identify faults and deviations from the expected path of maturation, and to select a specific maturation point at which a whisky can contribute to the blend. Blenders use a system of flavor descriptions to assist their work, but their method is largely to compare samples with experience or with a reference. Each sample is evaluated in terms of its similarity to an expected or acceptable product.

Raw Materials

Cereals

Raw materials account for about two-thirds of the cost of making malt and grain whisky. In the Scotch whisky industry, trading in malt and cereals is generally on the basis of analyses carried out under the *Recommended Methods of Analysis* (Institute of Brewing, 1997).

Unmalted cereal for grain distilling is traded on easily measured qualities, such as moisture content, specific weight, sieve analysis, and nitrogen content. It may also be analyzed to

determine its alcohol-yielding potential, either calculated from starch content, or from trial fermentations in the laboratory.

Malt for grain distilling is primarily considered on the basis of diastatic activity. The α- and ß-amylase contents are analyzed by measurement of dextrinizing units and diastatic power as detailed in *Recommended Methods of Analysis*. Malt for the production of malt whisky is considered on the percentage of hot-water extract. Predicted spirit yield in liters of alcohol per metric ton may be calculated from the percent hot water extract, with account taken of differences in the fermentability of extracts by a standard laboratory fermentation (Dolan *et al.*, 1981). The levels of total and soluble nitrogen from malt are also important in assessing likely alcohol yield. Also included in malt specifications is the degree of modification, tested by means of the "friabilimeter" and expressed as both overall percentage friability and percentage unmodified grains. Other malt analyses that may be carried out because of possible effects on whisky quality include measurements of volatile phenols, sulfur dioxide, and nitrosodimethylamine (Hardy & Brown, 1989).

Yeast

Standard tests for yeast viability and counts of total bacteria can be used to monitor yeast quality. Tests using laboratory fermentations may be carried out by yeast producers or distillers.

Water

Monitoring of water quality, to ensure consistency of supply, should include microbiological and chemical analyses. Chemical analyses include tests for hardness, iron content, and ammoniacal nitrogen. This is especially important for reducing water, in which a high iron content or excessive hardness may result in discolored or opaque spirits. Microbiological analyses should encompass water used in cooling systems to test for the presence of algae, or other suspended material that may result in clogging of condensers (Hardy & Brown, 1989).

Mashing and Fermentation

Optimum mashing conditions are set either from laboratory trials, from controlled distillery trials, or from a combination of both. Mashing temperatures and pH are critical. The fineness of malt grind may be checked by sieving techniques. Hydrometer measurements for gravity determinations do not fully indicate the progress of mashing and may be supplemented by other measurements, such as analyses of, α-amino nitrogen content, pH, worts viscosity, sugar and residual starch composition, and enzyme activity (Hardy & Brown, 1989).

Fermentations are monitored in all distilleries by following the decrease in specific gravity. Supplementary monitoring techniques include analysis of pH, percentage total acid, and optical rotation (Dolan, 1976). Accurate measurements of both the concentration of alcohol in wash and the bulk volume of wash are essential to measure fermentation efficiency, and in malt distilleries, where a certain amount of alcohol is left behind during distillation, to check on distillation losses. Ethanol may be measured by hydrometers, pycnometers, density meters, and gas chromatography, although results of the latter are not accepted by many excise authorities. Samples with high levels of soluble solids, which can obscure direct alcohol measurements, must be distilled prior to analysis (Watson, 1993). High-performance liquid chromatography analysis may be used for the quantitative analysis of mono- and oligosaccharides remaining after fermentation (Honda, 1984).

Distillation

Alcohol measurement in spirit safes of batch stills for judging cut-points, relies on hydrometers calibrated in per-cent alcohol at 20 °C, and Celsius thermometers. Efficient recovery of ethanol in patent stills is achieved by ensuring that no ethanol leaves the still in spent wash or fusel oil. While the former may be determined with on-line sensors, the latter requires off-line monitoring, either by density-based techniques or gas chromatography.

Quality control of new-make whisky relies mainly on organoleptic assessment by panels of at least four or five trained assessors (Hardy & Brown, 1989). No other analytical technique is capable of guaranteeing spirit quality. On-line gas chromatography of specific constituents is used in some grain distilleries to give immediate warning of changes in spirit consistency. Off-line gas chromatographic analyses are widely used for determining the spirit composition before, during, and at the end of maturation. Typical analyses of Scotch malt new distillate are shown in Table 11–2.

Maturation

Traditional methods of following maturation rely on organoleptic assessment, spectrophotometric determination of absorbance at 430 or 525 nm, and determinations of levels of soluble solids, total phenols, and reducing sugars. Liquid chromatography may be used to measure sugars, furans, and lignin breakdown products such as vanillin (Watson, 1993). Analyses of the wood-derived components in a Scotch malt whisky are shown in Table 11–3.

Table 11–2 Composition of the major cereals used for production of whiskies

Period	*4*	*4*	*4*
Charge	12	14	16
Strength (% v/v)	63.5	71.5	69.4
Acetaldehyde	3.2	3.8	6.8
Ethyl acetate	23.7	25.5	27.0
Diethyl acetal	1.7	1.2	2.2
Methanol	5.1	4.6	5.3
Propanol	40.8	42.7	41.9
isobutanol	79.8	80.8	80.5
oa Amyl alcohol	47.7	44.7	49.5
isoamyl alcohol	142.5	145.5	142.5
Total higher alcohols	331.1	313.7	314.4
Ethyl lactate	4.7	2.5	4.1
Ethyl octanoate	1.6	1.9	1.7
Furfural	3.3	3.9	4.2
Ethyl decanoate	5.7	5.6	4.5
ß-Phenethyl acetate	5.7	7.5	5.9
Ethyl laurate	2.1	2.6	2.1
ß-Phenylethanol	3.8	0.6	0.6
Ethyl myristate	0.6	1.1	0.6
Ethyl palmitate	2.7	3.3	2.6
Ethyl palmitoleate	1.5	1.9	1.4

oa, optically active.
Concentrations are g/100 l alcohol.
From Nicol, 1989.

Table 11–3 Absorbance and nonvolatile compound concentrations determined by HPLC in Scotch whisky distillates from three cask types at 53.4 % and 67.5 % ethanol (v/v) after 36 months' maturation

	Ethanol (67.5 % v.v)			*Ethanol (63.4 % v/v)*		
	1	*2*	*3*	*1*	*2*	*3*[a]
Total phenolsl[b]	0.11	0.08	0.07	0.11	0.08	0.07
Galloyl esters[b]	12	8	7	11	9	7
Gallic acid	2.9	3.4	3.2	2.5	3.2	2.6
A_{520} ($\times 10^{-2}$)[c]	29	24	23	28	19	22
Vanillin	3.1	1.6	1.6	1.8	1.3	0.9
Syringaldehyde	8.0	3.7	3.0	8.8	3.0	2.6
Vanillic acid	2.0	1.0	0.9	1.1	0.9	0.9
Syringic acid	2.3	1.2	1.4	1.4	1.1	1.2
Coumaric acid	0.10	ND	ND	0.06	ND	ND
Ferulic acid	0.08	0.01	ND	0.03	ND	ND
Ellagitannins[d]	3.7	1.1	0.7	1.8	0.4	0.4
Coniferaldehyde[e]	4.0	0.7	0.7	3.3	0.7	0.7
Sinapaldehyde[e]	4.9	1.0	0.7	4.0	1.0	0.7
Elliagic acid[d]	0.6	ND	ND	0.6	ND	ND

ND, not detected.

Concentration given as mg/l.

[a]Cask types: 1, previously used for bourbon whisky; 2, type 1 subsequently used for Scotch malt whisky; 3, used several times and with little maturation potential.

[b]As gallic acid.

[c]Absorbance at 520 nm.

[d]Estimated from response factor for gallic acid.

[e]Estimated from response factor for ferulic acid.

From Piggott *et al.* (1993a).

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12

Rum

Denis A. Nicol

INTRODUCTION

The word rum conjures up sun drenched Caribbean beaches, lined with palm trees reflecting in deep blue seas, surrounded by coral fringed islands which make up the archipelago which arcs east and south, from Jamaica, Cuba to Trinidad and Tobago and thence to Demerara in Guyana on the north east shoulder of the South American continent.

Seventeen groups of islands contribute to more than two hundred and twenty different bottled rums, from straight pot and column distilled to blended and flavored rums, the products of more than fifty distilleries.

Rum is also produced on other continents and islands round the world wherever the latitude is favorable for sugar cane planting, associated with sugar mills attached to the estates or plantations. This chapter is compiled from knowledge gleaned from the Caribbean where the author has gained experience in traditional rum distilling.

THE HISTORY OF RUM

The subcontinent of India is the source of the first references to two liquors obtained from sugar cane. Written about 2000 BC, the sacred Indian Vedic texts, or 'The Vedas,' refer to a cane juice derived spirit called 'sidhu' and a molasses derived spirit called 'gaudi'. Another potable alcoholic product referred to as 'soma', was also available (Clutton, 1974).

'Like impetuous winds, like swift horses bolting with a chariot, the drink has lifted me up', Rig Veda.

It was known that Alexander the Great's armies sucked the tall stems of grass (cane) which gave forth a sap known as cane juice.

Sugar cane was also known to have been cultivated in China as far back as the second century A.D. The cultivation of sugar cane spread round the world and it was found in Madeira, Spain, Cyprus and Sicily, by the third century A.D. It was not until the end of the Middle Ages that the crop was farmed in the West Indies. Christopher Columbus has the distinction of introducing it to the Caribbean at the end of the fifteenth century (1493).

The production of distilled products from the sweet residues of the sugar mill process took some time to become universally established in the Caribbean. Barbados and Santo Domingo were the pioneers of modern rum production

with the colonization of the West Indies in the 17th Century.

Demerara, in what is now Guyana, boasts a distilling tradition stretching back to 1670 and it is likely that the practice extends before that. John French's "Art of Distillation", predates the establishment of Demerara rum production by nineteen years, being first published in 1651.

Around this time, 1650, a crude distilled product made from sugar cane was available under the name 'tafia' (Clutton, 1974).

Pot stills were used in rum production initially. Distillates required to be distilled several times to produce an acceptable potable spirit. Quality, health and safety factors were not overlooked even in these early days.

By the 18th century spirit produced from cane was now called 'rum' and Barbados, Jamaica, the Virgin Islands and Santo Domingo had established an expanding trade with Europe, especially Great Britain.

By 1753, Jamaica had developed an enviable reputation which continued through to the Philadelphia Exhibition of 1876 when its rum 'was unexcelled by that of any other country.'

It was the Spaniards in search of 'El Dorado' who colonized South and Central America, in their unstinting search for gold. Sugar superceded gold as the currency of trade in the colonies and further afield, as European powers fought to gain footholds on the islands of the Caribbean and the adjacent continental mainland. Thus Great Britain, France, Holland, Spain and Portugal established colonies in the Western Hemisphere; colonies were captured, bartered, traded and exchanged like commodities.

South America, Central America and Mexico remained under Spanish influence excepting Brazil, which was dominated by Portugal, and British Guiana, now Guyana. France and Holland had stakes in French Guiana and Surinam, respectively. The eastern Caribbean islands fell under British dominance, while others, to a lesser extent under French and Dutch dominion.

Rum had been produced in the New England colonies prior to the American Revolution of 1776. The British Parliament passed legislation in the 18th century called the Sugar and Molasses Acts. These acts placed restrictions on sugar and molasses imported into the North American colonies from the West Indies. The acts were part of the Acts of Trade and Navigation, a series of laws instituted by Great Britain to ensure the control of the commerce of the British colonies.

The New England colonies used molasses for the highly profitable business of rum manufacture. Molasses was available from either British or foreign sugar planters. The Molasses Act of 1733 was an attempt to force the colonies to buy from British planters or cease making rum (cf. Gin Act 1736). The colonists began smuggling supplies of molasses from the Spanish and French West Indies.

The Sugar Act of 1764 displaced the 1733 Molasses Act, when duty was raised on sugar and reduced on molasses; duty was added to Madeira wines and further duties were imposed on sea borne merchandise.

The taxation imposed by these acts is considered to be one of the indirect causes of the American Revolution (1775–1783); re Boston Tea Party. The rum produced in the New England colonies was exchanged for slaves to maintain the working establishment of the Caribbean; sugar, cotton and tobacco estates belonged to wealthy British families.

Negro slaves from West Africa were transported to the Caribbean, while the rum and sugar were exported to New England and Great Britain in a lucrative triangular trade which started in Britain; slaves were collected in West Africa and sold in the Caribbean or exchanged for sugar, molasses or rum; the ships laden with Caribbean produce returned to Britain via the American colonies where further exchanges took place. This trade continued until the American Revolution which had serious implications for merchant and seaman alike. Further problems awaited the British sugar planters when slavery was abolished throughout the colonies in 1834. The wealthy planters turned to the subcontinent of India for replacement labor.

Indentured laborers from the Calcutta region first made their appearance in the Caribbean and

Demerara sugar estates in 1838, a translocation which did not cease until 1917 (Williams 1977).

The manpower for running the sugar estates and adjacent distilleries in the Caribbean and Demerara was initially derived from slave labor. It was from this trade in human misery that sugar, molasses and rum had their manufacturing origins in the Caribbean.

THE ORIGIN OF THE WORD 'RUM'

As with many alcoholic beverages, the origins of their names are steeped in legend and mystery. Four roots for the word, rum, are given below.

Sugar, in Latin, is 'Saccharum', an acceptable etymology for rum.

'Rumbullion' in Devon meant a great tumult as also the word 'Rumbustion'. Both these Devon vernacular words, carried by sailors from the West Country to the Caribbean, are contenders for the origin of the word.

The Spanish word for rum is 'ron'. The Spaniards were distilling 'ron' in the West Indies long before Britons set foot in the Caribbean. Rum may be considered to be a corruption of the Spanish word 'ron' (Clutton, 1974).

It is a matter of personal taste as to which etymological root is chosen.

CANE JUICE PRODUCTION

Having established that cane sugar production provides molasses, the main raw material for rum manufacture, it is essential to dwell for a time on the process from which the molasses is derived.

As previously mentioned, the islands of the Caribbean are home to many sugar estates or plantations; the coastal plain of Guyana (Demerara) boasts many estates which feed cane to several sugar mills. Formerly each estate possessed its own rum distillery which processed the cane juice or molasses into alcohol.

Sugar cane (*Saccharum officinarum*) is an erect tall tropical grass (Fig. 12–1) first thought to have been introduced to the West Indies by Columbus. As mentioned above, it was already known to the East Indians as early as 2000 BC.

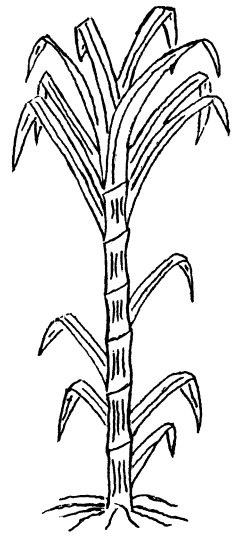


Figure 12–1 Sugar Cane - *Saccharum officinarum*

On crushing the stems (2–4.5 m long), each stem will release 15–16 % sucrose solution. One hundred tonnes of cane will yield an average of 10 tonnes of 96 degree sugar, at a yield of 10 % w/w. One hectare of plantation will deliver 60–70 tonnes of cut cane. Sugar mills, depending on capacity, can mill 100–200 tonnes of cut cane per hour. A cane ripener is normally applied to the crop some 5–6 weeks before harvesting to promote ripening by suppressing photosynthesis in the leaves. Proprietary cane ripeners are Touchdown or Fusillade; ripeners act by encouraging concentration of sucrose in the cane stem.

At the time of harvesting, the cane fields are set alight in a scorched earth policy to sanitize the soil; this scorches the stems of the cane plants sugar cane which are not immune from the heat; harvesting is effected by cane cutters wielding machetes. Sugar cane harvesting is thus very labor intensive. Hand won sugar cane is superior to that which is mechanically harvested. Like the hand winning of peat in the Highlands and Islands of Scotland, a better quality product is thought to be obtained.

The canes are topped to remove the leafy remnants and the cane is transported to the sugar mill by tractor and trailer. In Guyana, punts, which hold six tonnes of sugar cane each, are delivered to the mills by a series of crisscrossing canals on which mills are located. The canals and other trenches act as irrigation for the sugar cane plantations and are an unique feature of the Guyana subsea level landscape, effective in labor and transport costs. Selected cane tops are used for future planting.

Once cut, cane quality rapidly deteriorates. Disease, pests and weather are the enemies of cane prior to harvest. Post harvest, cane loses 1–2 % moisture daily for the first week. The scorching of cane, before cutting impedes water loss. Invertase, present in the juice, within the cane, inverts the sucrose to fructose and glucose, lowering the juice quality (Chen, 1985).

Leuconostoc mesenteroides, a soil contaminant, invades the cut cane. This bacterium is responsible for souring, and transforming the sucrose into the polysaccharide, dextran, a gummy material which creates sugar extraction problems and also affects molasses quality.

The time between the cutting and delivery of the cane to the sugar mill is critical. Dextran formation increases after cutting so that it is essential that newly cut cane is milled within twenty four hours of harvesting; some authorities suggest fourteen hours.

Burning cane prior to harvesting is not risk free and some damage may result with loss of sucrose if this act is not carried out carefully.

In the milling, extraction, clarification and crystallization processes, dextran causes loss of sugar, poor recovery, increased viscosities, filtration difficulties and indifferent molasses quality. Sugar crystal filtration is impaired by the formation of elongated needle like crystals, rather than the normal cubic crystals.

Having harvested fresh sugar cane and promptly delivered it to the factory, the sugar milling process is given in simple outline in Fig. 12–2.

MOLASSES

The sugar miller will expect to recover 4–5 tonnes of molasses from every one hundred tonnes of cane milled.

Selection of molasses for rum production depends on quality and price. Although total sugars are the most important parameter in molasses at say 55–56 % w/w and as invert at 52.2–53.2 % w/w, other factors also impact on molasses quality—

1) Sulphated ash	less than	8.0	%	w/w
2) Nitrogen	between	1.0–1.5	%	″
3) Gums	less than	2.0	%	″
4) Unfermentables	less than	3.0	%	w/w

The concentration of the constituents of molasses are dependent on cane variety, soil type, climatic conditions, cultivation methods, harvesting, milling and sugar recovery techniques (Chen, 1985).

Table 12–1 (Arroyo, 1947) gives analytical comparisons between good, poor and indifferent molasses.

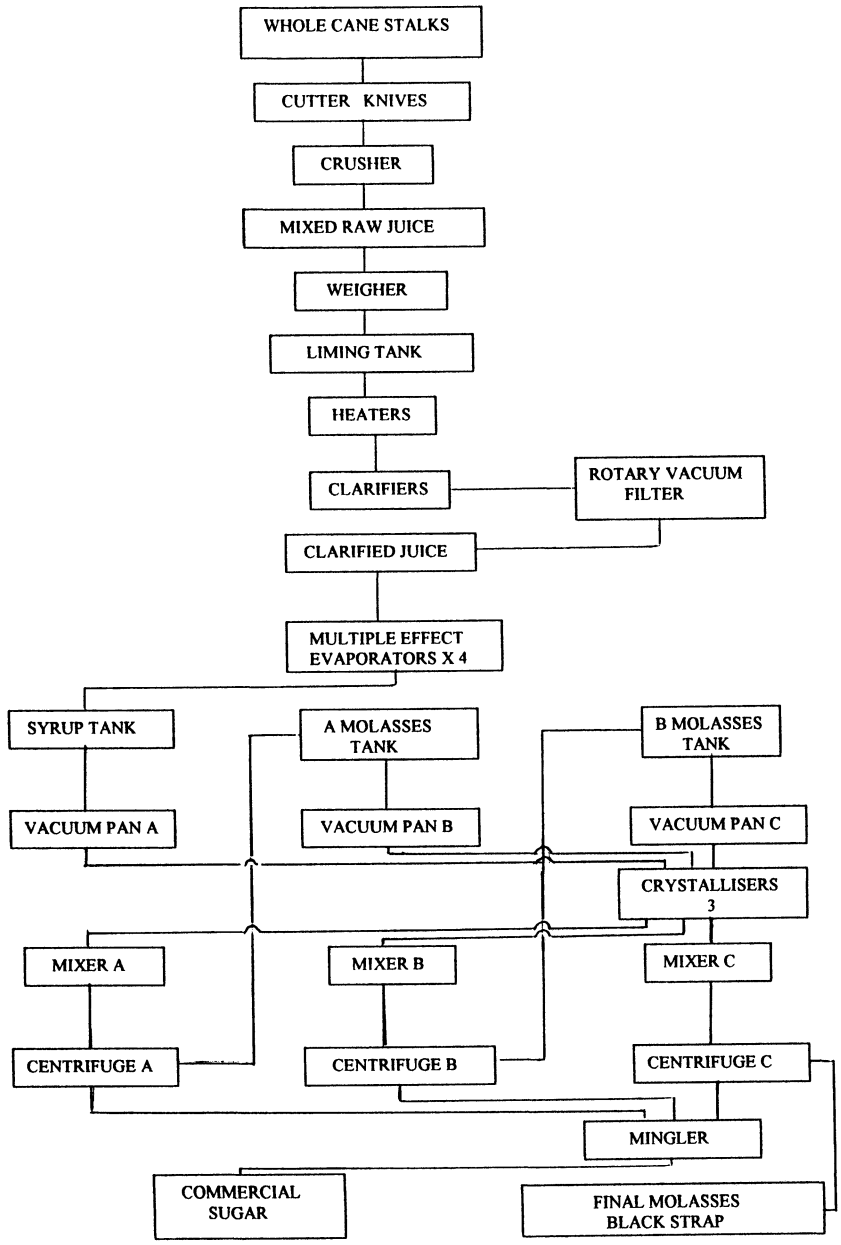


Figure 12–2 Sugar Mill Layout

MOLASSES HANDLING

Molasses, straight from the mill is delivered hot to the distillery, either directly by pipe from the mill or by road tanker. It can be accumulated in large storage tanks from coastal tanker deliveries, for further distribution by sea or road depending on the destination. The uses of molasses are legion such uses being outwith the remit of this chapter.

Table 12–1 Molasses Analyses

	Typical Analyses of Molasses for Rum Production		
	Good	*Fair*	*Bad*
Brix Density	87.6	85.4	88.2
Total Sugars As Invert (FSAI)	57.97	52.91	49.93
Sucros	36.44	31.30	34.61
Reducing Sugars	19.61	19.96	13.50
Ash	7.31	9.35	11.57
Total Nitrogen	1.10	0.60	0.45
Total Phosphate	0.19	0.09	0.21
Gums	5.5	5.7	6.3
TSAI: Ash Ratio	7.93	5.65	4.61
Reducing Sugars: Sucrose Ratio	0.54	0.64	0.39
Phosphate: Total Nitrogen Ratio	0.17	0.15	0.47
Gums: TSAI Ratio	0.03	0.05	0.08
Aroma by Steam Distillation	Good	Fair	Indifferent

Results expressed as percentage weight for weight

Molasses delivered into a distillery should be weighed in rather than be accepted on a volumetric basis. Molasses delivered by volume is subject to volume and density variations due to temperatures which can vary from 45–65 degrees Celsius. Elevated temperatures and especially temperatures exceeding 60 degrees Celsius, thermally degrade the molasses through Maillard reactions with sugar losses. It has been known for molasses under high temperature storage to spontaneously combust in runaway exothermal reactions leaving but charred remains. Ideally, molasses should be stored at around 45 degrees Celsius (Chen, 1985).

Positive displacement pumps are used for transferring the hot molasses at 85–88 degrees Brix. Following in line mixing with water there is a rapid decrease in viscosity and centrifugal pumps can be used. Electronically controlled proportional in line mixers are used to blend water and molasses to the desired working specific gravity. Electronic volume controllers ensure that each fermenter receives the correct set volume of diluted molasses. In line density meters record the specific gravity of the diluted molasses as it passes to the fermenters.

Molasses, as delivered, possesses a density 1.5 times that of water and requires to be stored in tanks which allow for this. If water tanks are used, they should not be filled more than two thirds full to compensate for the high density.

Vessels and pipework designed to hold and transfer molasses can be fabricated in mild steel but the use of stainless steel ensures improved hygiene and eliminates corrosion.

The purchase of molasses should be based on total sugar content and not Brix, as the correlation between Brix gravity, specific gravity and sugar content is poor.

The world molasses trade centers on New Orleans, Louisiana. Molasses prices are generally quoted on the basis of f.o.b. New Orleans, per tonne at 79.5 Brix and with about 45 % Total Sugars as Invert (TSAI).With the advent of High Performance Liquid Chromatography (HPLC), it is now possible to analyze molasses for sucrose, glucose and fructose. New Orleans molasses merchants are now accepting contracts to sell molasses to distillers on the actual sugar concentration rather than on TSAI, although both analyses are acceptable (Murtagh,1995).

CANE JUICE

Cane Juice can be used as a source of fermentable sugars for the production of lighter flavored rums. With a sugar content of 12–16 % w/w sucrose, cane juice can be used directly in the fermenters and does not possess the high level of suspended solids, which, in molasses, foul the internal distillation surfaces. Susceptible to infection, cane juice must be used immediately on extraction as it possesses a large flora of yeasts and molds. Storage encourages the development of bacteria and spontaneous fermentation is not uncommon.

DIFFERENT TYPES OF MOLASSES

There are at least six basic types of molasses, which can be used for producing alcohol (Murtagh, 1995).

a) Blackstrap molasses
b) High Test Molasses from evaporated cane juice
c) Refiners cane molasses
d) Beet molasses
e) Refiners beet molasses
f) Citrus molasses

In relation to rum production, only the first three molasses, a, b and c can be used.

YEASTS

Formerly rum fermentations could be allowed to progress naturally with the aid of the ubiquitous yeasts and bacterial flora and fauna derived from the atmosphere, present in the water or lying dormant in the molasses.

Today, although such an age old traditional technique, as briefly described above, may now be employed for specific rums, it is more likely that pure culture yeasts are used in fermentations.

Thus, Saccharomyces cerevisiae, Sacch. bayanus or Schizosacharomyces pombe now play their roles in rum fermentations along with various strains of competing bacteria. Dunder, as a naturally developed inoculum for fermentations containing wild yeasts and anaerobic bacteria, can be employed to enhance and provide increased congeners. Dunder is the residue of wash distillations and it is allowed to ferment naturally in a 'dunder pit', prior to its use as a fermentation inoculum or an additive to wash or alcohol in a pot still.

YEAST PROPAGATION

A selected strain of yeast is usually cultured from slopes, lyophilized cultures or specially prepared active dried yeast in the laboratory. Through serial preparation it is processed into final bub ready for fermenter pitching in three to four days. Propagation commences in the laboratory using a dried culture of Sacch. cerevisiae. A given weight of dried yeast is suspended in a mixture of warm water and cane sugar in a flask. The contents of the flask are allowed to stand for 15 mins, prior to inoculating yeast vessels or bub tanks.

Sterilized wash at normal fermentation gravity, 16–18 degrees Brix, is used as the culture medium for the inoculum, the amount of inoculum depending on the receiving volume.

Each stage is carefully monitored to ensure maximum growth of yeast under aerobic and aseptic conditions. The medium, molasses at 18 degrees Brix initially, is sterilized by heating to and holding at 100 degrees Celsius for a specific time, before cooling to 30 degrees Celsius, prior to inoculation. The molasses used is treated with sulfuric acid to reduce the pH to between 4.5–4.8 which suppresses bacterial growth; while ammonium sulphate, a nitrogen source at 0.03–0.06 % w/v is added to stimulate yeast growth.

When the Brix level in propagating vessels and bub tanks drops by 5–6 degrees and the yeast cell count reaches 2.0×10^8 yeast cells per ml, the next larger volume vessel is inoculated, until three to four days from the initial preparation, a fermenter is available for pitching with yeast bub. Incremental feeding of the partly utilized sugars in the bub tanks with sterilized wash

can help to maintain the culture. As most distilleries are situated in tropical countries, it is more convenient to use dried yeasts, especially baker's yeast as the active fermentation ingredient. The temperature of the fermenting media at all stages should be maintained at not more than 30 degrees Celsius.

As with all propagation plants, where the desired end product is an aseptically produced yeast, the strictest attention to hygiene and sterilization techniques is essential for satisfactory results. Yeast health and vitality, not to mention viability, can be affected by certain compounds within the molasses. The by products of overheated sugar: 5-hydroxy methyl furfural, condensation products, the results of browning reactions, can adversely affect yeast performance. HMF in excess of 500 ppm (0.05 % w/w) and certain volatile fatty acids- acetic and butyric are toxic to yeast (Lehtonen & Suomalainen, 1977).

FERMENTATION

Fermentation is usually carried out in either cylindro-conical fermenters with domed tops which facilitate in place cleaning or carbon dioxide recovery, where this is carried out, or in cylindrical open topped vessels with sloping bases. As dead or final wash contains a high level of suspended solids originating from the molasses and yeast cells, it is wise to make allowances for these solids in fermenters, wash chargers and distillation beer wells, by judicious design. Suspended solids presented to the wash stills can cause severe fouling (Murtagh, 1995).

A fermenter (100,000 litres capacity) is inoculated with active yeast from the final bub tank as the fermenter is filling. A proportional water/ molasses in line mixer ensures that the setting Brix is in the desired range 16–20 degrees Brix, 1064–1080 of a specific gravity which the yeast should ferment comfortably. Temperature control is very necessary, as final fermentation temperatures are a function of the sugar concentration and ambient temperatures which are in the range of 25–32 degrees Celsius. Thus fermentation temperatures are maintained at 30–33 degrees Celsius. Cooling is performed by external heat exchangers, internal cooling coils or water jackets. For conservation purposes, water is usually circulated through a cooling tower. Molasses fermentations proceed at a very high rate—within 24 hours fully attenuated wash is produced, yielding 5–7 % alcohol by volume depending on the original setting gravity. High gravity fermentations can be pursued where energy and effluent savings will be a bonus; such fermentations can produce alcohol concentrations of 10–13 % ABV. Without pre fermentation wash clarification, final gravities of less than 1028 to 1032 (7–8 degrees Brix) will not be achievable. Pretreatment of diluted molasses prior to fermentation requires the addition of ammonium sulphate (0.03–0.06 % w/v) as a nitrogen source and sulfuric acid (SG 1.83) to reduce the pH. A 0.02 to 0.04 % w/v of sulfuric acid addition is usually sufficient.

Suspended solids can be partially removed from the molasses prior to total dilution and fermentation; the molasses is first diluted to 45.0 degrees Brix, then the temperature is raised to 70.0 degrees Celsius to pasteurize the molasses. The sulfuric acid is added at this stage as it encourages sedimentation. The diluted and acidified molasses is transferred into a large settling tank, designed in such a way that the precipitated sludge can be decanted from the conical base; the supernatant, clarified molasses, is further diluted to the desired gravity and pumped to the fermenter where it is dosed with nutrient and pitched with yeast. Although the yeast will contribute to the fermenter solids, improved fermentation should ensue and dead wash handling will be simplified; the impact of the original calcium salts, especially gypsum, on the sieve plates, caps and heating surfaces in both pot and column stills should be reduced, resulting in less downtime for cleaning.

Fermenters are usually constructed of wood, stainless steel, mild steel or even glass reinforced fibre.

From a hygienic standpoint, stainless steel is the material of choice.

FERMENTATION EFFICIENCIES

It is normally expected that fermentation efficiencies of 80–85 % will be achieved in the distillery. Bacterial contamination via Lactobacillus and Leuconostoc spp is not uncommon, interfering with alcohol production. The strictest control of hygiene relating to raw materials, that is, yeast, water and molasses reduction, fermentation vessels and ancillary pipework is essential; the hygiene regime should incorporate the yeast propagation plant–vessels as well as bub tanks and pipework. Where it exists, CIP units should be used to their fullest using the correct combination of chemical cleaning agents, caustic soda for removing soil and sodium hypochlorite for sterilizing. Where no CIP exists, high pressure hose systems with chemical dosing features should be used. Undivided attention should be paid to plant design characteristics to eliminate bacterial havens—

- fermenter coolers,
- suppurating dead legs,
- valve bodies,
- fermenter vents,
- overflow pipes,
- fermenter vacuum/pressure pots,
- door seals,
- fresh/dead wash transfer lines,
- yeast transfer lines,
- any offending appendages.

Attention to detail is a necessity for achieving maximum alcohol and eventual distilled spirit yields, which can be easily denied through poor hygiene. The use of palm oil or other vegetable oils, vulnerable to rancidity caused by infection, should not be used to suppress wash foaming. Silicon antifoams of food grade quality should be used to avoid introducing unnecessary infection and avoidable spirit off notes.

Table 12–2 shows the impact on yield of a tonne of molasses containing 51.1 % total sugars subject to reasonable fermentation efficiencies. Distillation efficiency is expected to be at least 97.0 %.

To understand the biochemical relationship between fermentation and alcohol, it is necessary to examine the stoichiometric equation.

$C_6H_{12}O_6 \rightarrow$		$2CH_2CH_2OH +$	$2CO_2$
Glucose		Ethanol	Carbon dioxide
MW	180	92	88
Kg	1000	511	489

Table 12–2 Calculation of Distillery Efficiencies

% Total Sugars in Molasses		50.1
Molasses °Brix		87.0
Per cent total sugars less per cent non-fermentable sugars	=	fermentable sugars
50.1 less 3.0	=	47.1

1000 kg (tonne) molasses at 47.1% fermentable sugars contains 471 kg. fermentable sugars.

471 × 0.511 (Gay Lussac Yield) yields	=	240.73 kg ethanol
240.73 × 0.95 (Pasteur Yield) gives	=	228.69 kg. ethanol
228.69/0.7894 (SG 100% ethanol)	=	289.70 litres pure alcohol per tonne (theoretical yield in LPA / Tonne)

With an assumed fermentation efficiency of 82.0% and a distillation efficiency of 97.0%,
Overall Plant Efficiency is (82.0 × 0.97)% = 79.54%

$$\text{Potential Distillery Yield} = \text{theoretical yield} \times \text{plant efficiency} = \frac{289.7 \times 79.54}{100} = 230.43\text{LPA/tonne}$$

Yield factor, based on fermentation efficiency of 82.0% is 0.4891
Potential yield per tonne of molasses is 471.0 kg fermentable sugars × 0.4891 = 230.37 LPA/t molasses or the reciprocal 1/0.4891 = 2.045. LPA / tonne = 471.0 / 2.045 = 230.32.

For the inversion of sucrose, the equation is

$C_{12}H_{22}O_{11}$ + H_2O → $2C_6H_{12}O_5$		
Sucrose	Water	Invert sugar (fructose and glucose
MW 342	18	360
Kg. 1000	52.6	1052.6

Invert sugar multiplied by 0.95 gives the original sucrose content.

The invert sugar in molasses contains about 3–4 % unfermentables.

Thus a molasses containing Total Sugar as Invert (TSAI) of 53.5 % will have

$$1000 \times (53.5 - 4.33) / 100 = 491.17 \text{ kg}$$

fermentables per tonne of molasses.

From the stoichiometric equation,

$$491.17 \times 0.511 = 250.99 \text{ kg ethanol}$$

Invoking the Pasteur Effect,

$$250.99 \times 0.95 = 238.44 \text{ kg ethanol}$$

At 80 % Fermentation Efficiency (F.E.) $238.44 \times 0.80 = 190.77$ kg ethanol, the SG of 100 % alcohol is 0.7894, 190.77/0.7894 = 241.64 LPA/t

The distillation efficiency of 97.0 % reduces this to 241.64×0.97 to 234.39 LPA/tonne.

For a fermentation efficiency of 80 and a distillation efficiency of 97 %, dividing the fermentable sugars per tonne by the factor 2.095 will give the potential yield.

i.e., 510 kg sugars/2.095 = 243.4 PA/tonne.

It is possible to vary the parameters—fermentable sugar content verses efficiencies and predict spirit yields.

DISTILLATION

The word rum, first coined in the Caribbean, has become generic; rums are produced in many tropical and subtropical countries round the world, where molasses is available from the mills of the sugar growing areas. Hence rum stills of many different designs can be found in Colombia, Venezuela, Brazil, Ecuador, Peru, Bolivia, Spain, USA, Australia, India, Philippines, Indonesia, Thailand, Madagascar, Swaziland, South Africa to name but a few countries producing rum, ron, agua ardiente or even gasohol.

The Caribbean remains the closet of some very traditional distilling plant and stills are to be found made of copper and wood, both pot and continuous although stainless steel has made its intrusion into these havens of tradition. Pots are of coopered wood, upon which sit the copper shoulders and swan neck. The pot still can be of a single (Fig. 12–3) or a double (Fig. 12–4) pot distillation arrangement where the double pot has two wash stills in tandem; the vapor pipe of the single pot still is extended into a retort, on which sits a rectifier; from the rectifier, a vapor pipe leads to a worm tub or shell and tube condenser, the tail pipe servicing a test case or spirit safe which feeds the appropriate receivers, low wines or spirit. The stills are fired indirectly by steam or directly by bagasse, the dried residue of the sugar milling operation if readily available. Bagasse is used to produce high pressure steam in the mills to drive steam engines for milling and generate electricity through steam turbines (Chen, 1985).

Column stills are commonly used; these are constructed of stainless steel and copper. One distillery boasts the world's last remaining operational Coffey still (Fig. 12–5) as originally designed by Aeneas Coffey. Made of wood and copper, it posses an analyzer and rectifier to the 1830 design. The product obtained is unique but the maintenance costs are high and the still could well be relegated to a museum.

Unlike Scotch whisky production, stills are expected to produce different products from the same still, especially column stills, where conditions are adjusted by controlling the distillation parameters to alter the congener balances, producing distillates with different congener complements. Such distillates are given their own designation and these are used to produce different blends.

The pot stills, as expected, produce more robust, heavier rums, requiring prolonged maturation, similar to malt whiskies.

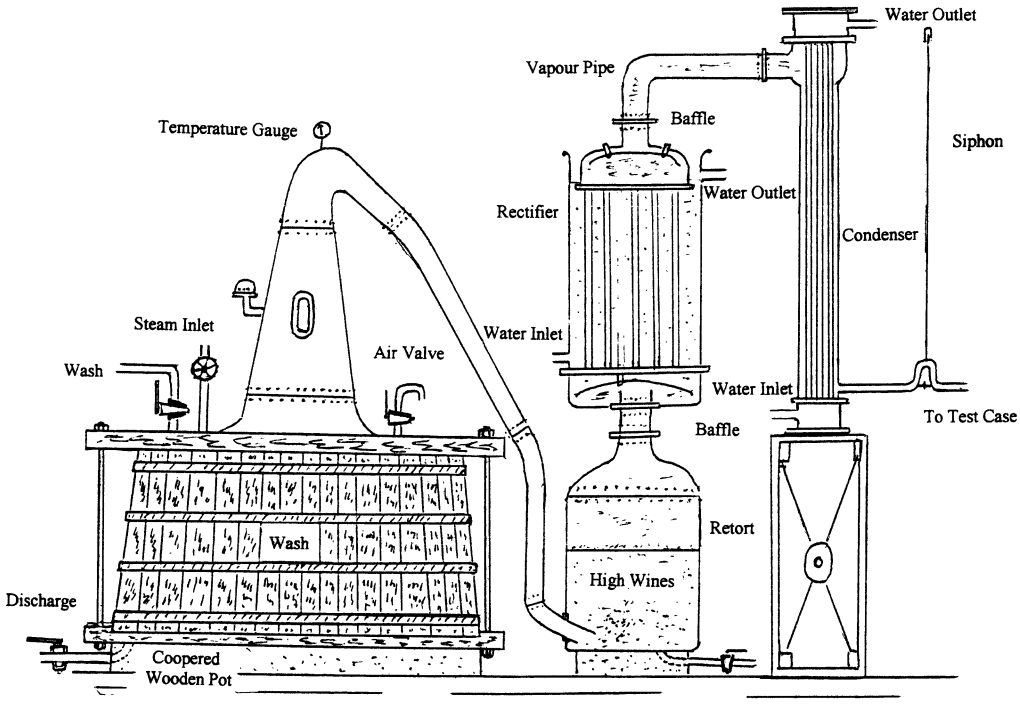


Figure 12–3 Single Rum Pot Still

Column stills, in comparison, produce light rums and with the correct column configuration, neutral spirits for gin and vodka production.

Distillates are collected between 80–94 % ABV for the rums and > 96.0 % ABV for neutral spirits.

High ester rums are in a unique category, being much in demand for enhancing flavor.

POT DISTILLED RUM

It is worthwhile dwelling on the practical production of pot distilled rum.

The still consists of a traditional pot of copper or coopered wood construction, similar to a wooden spirit receiver or washback in a malt distillery; it may possess a wash preheater of plate and frame design and is usually heated by steam coils or pans. The vapor section of the still, swan neck, lyne arm (vapor pipe) and other ancillary equipment is fabricated from copper and brass. The lyne arm extends from the head of the still to the base of a retort on which sits the rectifier. The retort and the rectifier may be an option and in some stills, of more simple design, these units may be omitted.

Where the retort is used, another vapor pipe extends from its top to a shell and tube condenser.

The retort is a cylindrical vessel, which is filled with low wines; the rectifier is a cylindrical water container, through which a series of wide bore copper tubes pass. The vapors from the retort pass through the tubes via a baffle plate and exit to the outgoing vapor pipe via another baffle to the condenser, via another vapor pipe. In effect, the rectifier acts like a condenser with the roles of the tubes reversed.

The pot is charged with wash ~ 5–7,000 litres at 5.5 % ABV. In addition, the retort is charged with low wines at around 51–52.0 % ABV, derived from previous distillations.

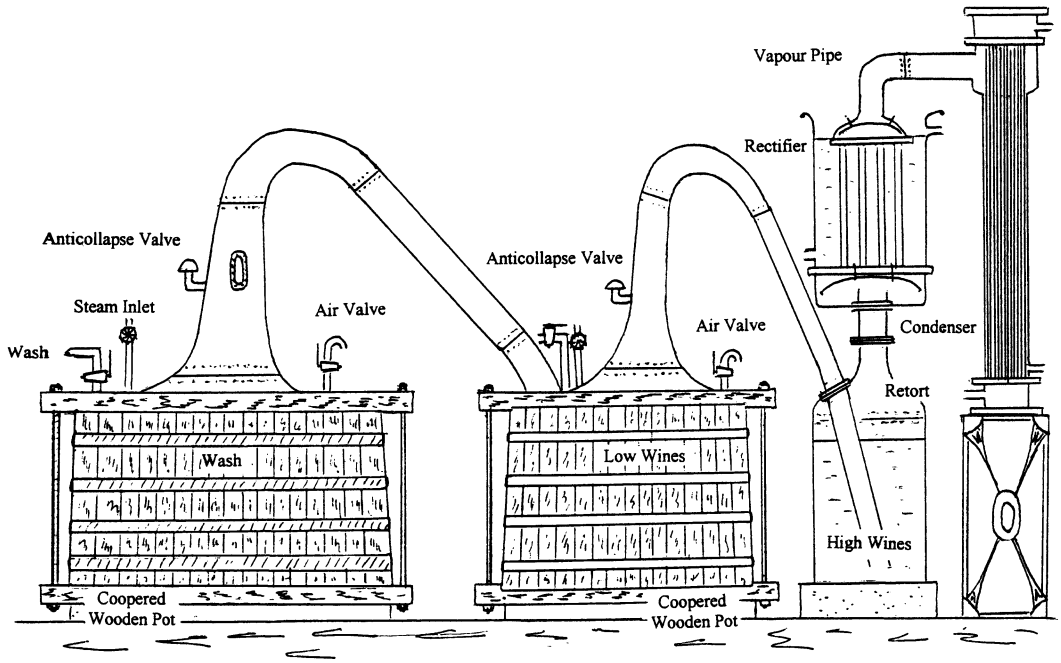


Figure 12–4 Double Rum Pot Stills

Distillation commences in the pot still; the hot vapors from the boiling wash climb up the swan neck, through the head and descend into the retort, where the submerged vapor pipe injects the latent and sensible heat into the low wines. The boiling retort contents, encouraged by the hot vapors from the still ascend through the rectifier tubes. By deft manipulation of the energy input and the supply of water to the rectifier and condenser, the quality of the ensuing spirit can be controlled. The water temperature in the rectifier is controlled at 45–50 degrees Celsius. The subdued vapors, with their compliment of permitted congeners, finally condense, exiting either briefly as heads, then low wines, spirits and feints.

For the first five minutes of distillation, the heads, cloying with esters, are collected in the low wines receiver at 88 % ABV.

The flow is directed to the spirit receiver, spirit being collected over a period of 1½ to 2 hours at a strength of 85.0 % ABV and a volume of 360–370 litres. The spirit run continues until the strength drops to 43.0 % ABV, and the flow is directed to the low wines receiver, as feints. Distillation is completed when the distillate strength approaches 1.0 % ABV. The average strength of the low wines is 51.0 % ABV. The low wines collected act as the next charge for the retort for the following batch distillation.

Such a technique, as outlined above, produces a unique full bodied pot still rum.

A similar apparatus for producing another type of pot distilled rum consists of a pair of pot stills in tandem, each charged with wash contained in an all copper or copper/coopered wooden pots. The extended vapor pipe of the first wash still penetrates the shoulder of the second wash still down to the base of the pot. Each still is provided with steam coils or pans. Essentially, the first wash still drives the second still; as above, the second still's vapor pipe or lyne arm enters the retort, projecting to its base; the rectifier again sits astride the retort. The vapor pipe from the rectifier is led to the condenser and the heads/spirit/low wines tail pipe to the low wines and spirit receivers via the test case.

The volume of wash in the first pot can be as much as 15,000 litres and in the second pot,

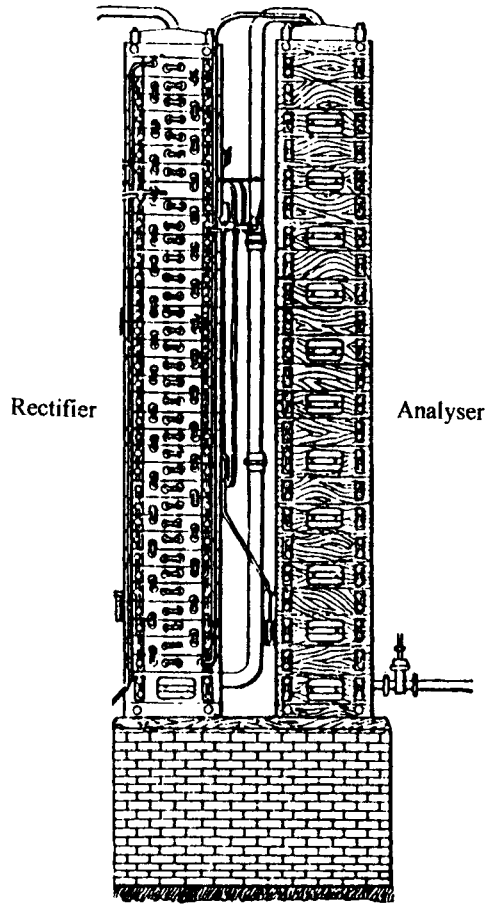


Figure 12–5 Original Coffey Still

10,000 litres. A similar procedure is adopted for producing this type of pot distilled rum from 5–6 % ABV wash, as described for the single pot unit. Again, a unique product is produced.

Distillation cycles are in the order of eight hours.

Remnants of spent wash or lees from the retorts are discharged to sewer.

The rectifier plays an important role in molding the strength and character of the distillate.

The reflux is affected by the flow rate and temperature of the cooling water. Too much cooling and the rectifier may act as a reflux condenser, with no spirit escaping; too little water and the distillate flow rate will be adversely affected, containing higher boiling congeners, the result of reduced reflux. The stillman has to maintain a delicate balance between distillation rate, controlled by the still heat input and the amount of water required to effect a satisfactory reflux, to collect a spirit of the desired bouquet.

Formerly, pot distilleries were associated with small cane farmers who produced the local Caribbean 'tafia'.

HIGH ESTER RUMS

Another form of pot distillation produces high ester rums. The feed stock for processing this rum is a combination of naturally fermented 'dunder', derived from stillage and 10 % ABV.

Still bottoms—stillage, are placed in a dunder pit, a covered hollow in the ground, and allowed to undergo natural fermentation. Wild yeasts and anaerobic bacteria produce a range of volatile fatty acids and esters, predominantly butyric and acetic acids. The anaerobically produced acids may be fixed with lime, to promote the growth of aerobic acetifying bacteria, essential for acetic acid production.

The charges to the first still comprises a mixture of fermented dunder and alcohol, with the resultant charge being 10 % ABV; the second still is charged with low wines and the third with high wines. The recipe can be varied according to the desired end product. The configuration is similar to a double pot apparatus as described above, but without the rectifier. High ester low wines are charged into the low wines still and high wines into the high wines still.

Distillation is allowed to proceed. The contents of the stills are recycled for up to six hours. The mixture of acids, butyric, valeric, caproic, caprylic, acetic etc., are esterified by the added ethanol. Copper acts as a catalyst and the final spirit, when it is eventually drawn off, possesses an ester content in excess of 2000 g/100 LPA.

The product, with its unique, unmistakable bouquet is much sought after by flavor houses, rum and tobacco blenders.

COLUMN DISTILLATION

Serious alcohol producers associated with several sugar plantations and a seemingly endless supply of molasses resort to using continuous distillation columns.

The theory of continuous distillation has been discussed elsewhere and need not form part of the following description (Nicol, 1989 & 1993, Murtagh, 1995).

One company boasts a wooden Coffey still, as previously mentioned. Entirely made of wood and copper, it has withstood, remarkably, the ravages of time and is a unique and 'shining' example of an original Coffey still—reputed to be the last remaining working still of its type in the world. The rectifier contains sieve plates and the serpentine of copper coils, which preheat the wash, while the analyzer possesses a series of copper sieve plates, sandwiched between the wooden frame.

A two column patent still of French Savalle design can also be employed to produce at least six different products, from light to medium flavored rums to rectified spirit. By manipulation of feeds and columns, analyzer, aldehyde, rectifier and purifier, it is possible to reproduce products of long discontinued, dismantled or redundant distilleries, whose names live on in the abbreviated designations given to each product.

Trapezoidal tunnel caps, bubble caps and sieve plates are used for vapor/liquid enrichment in the columns. The tunnel caps can be easily removed for descaling, when calcium sulphate deposited from the wash eventually fouls the boiling or analyzer columns. Chemical agents are available for descaling to reduce the need for the laborious manual cleaning.

'Coffey' stills of tubular design mimic the contortions of the original Coffey still, the supporting wooden frame being replaced by a cylindrical column of copper and stainless steel.

The stills are made of a mixture of copper and stainless steel; the copper is strategically placed to assuage the adverse effect of volatile sulfur compounds on the quality of the final spirit, such compounds being abundant in molasses fermentations.

The strength of products from continuous stills varies from 92.0 % ABV (Coffey still) to 96.6 % ABV in stills of a Tri-Canada design.

Spirit take off is within the range of 25–50,000 LPA per day, depending on the design capacity of the still.

In a typical distillery (Fig. 12–6), a 168 hour week can provide 60 × 100,000 litres fermentations or six million litres of wash at 7.0 % ABV. At a yield of 250 LPA/tonne of molasses, this amounts to the use of 1680 tonnes of molasses per week delivering 420,000 LPA.

As in malt distilling, a pot still will have a tenth of the output of a continuous unit.

Sugar production revolves round crops of sugar cane of which there are usually two per annum; the supply of molasses is dependent on the milling periods, when the cane is harvested. It is therefore possible to have the equivalent of

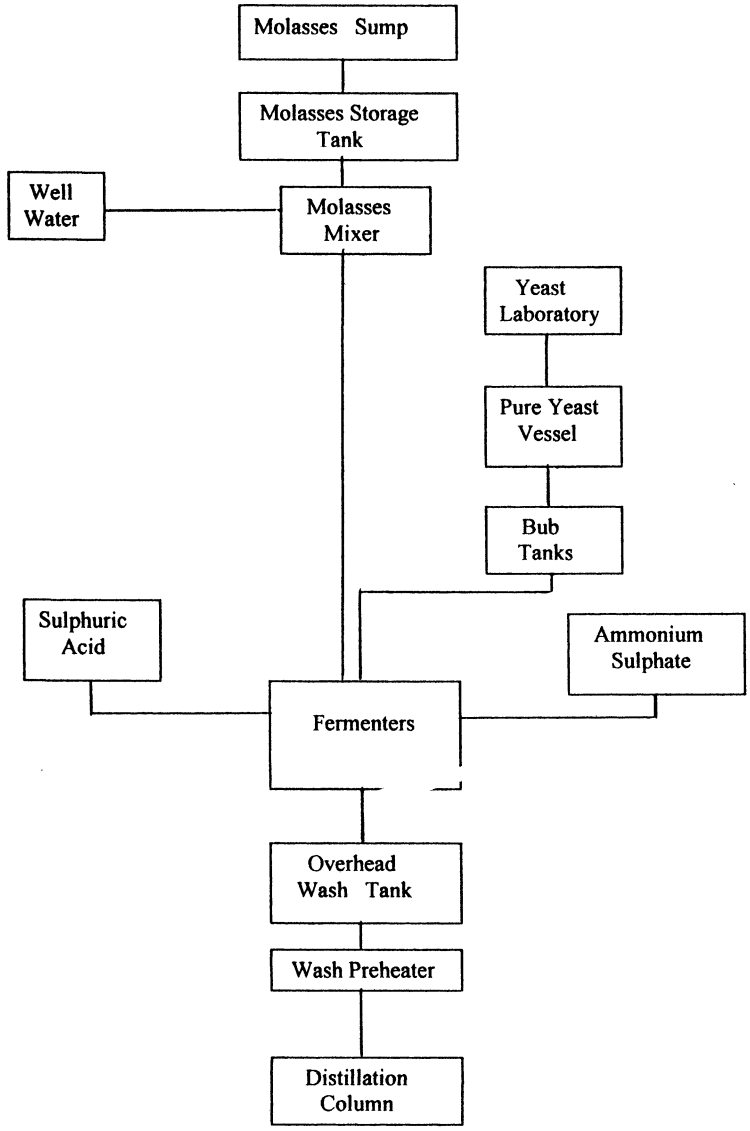


Figure 12–6 Continuous Still Layout

two 'silent seasons' or maintenance periods when molasses is not available.

INVENTORY CONTROL AND MANAGEMENT

The control of maturing casks and fillings, predicted market growth expectations over many years for aged rums demands a good knowledge of the external market.

Annual growth estimates impact on distillery production levels, the purchase of casks for new fillings, and warehouse space required for maturation.

A cask policy must be established meets the demands of the different types of rums. When casks become totally exhausted, there should be

a purchase procedure to replace such casks to meet immediate and future requirements.

Most rum distillers use American barrels, or remade American barrels risen from shooks. Aged rums which are laid down for several years may require to be matured in fresh Bourbon casks, while light rums possessing few congeners can be matured in well used, but not quite exhausted barrels.

Charred and decharred casks can be used to impart the desired nuances of flavor on similar rums for future blending.

Before filling, casks should be nosed to determine freshness; tainted or sour casks will adversely affect maturing spirit. One organoleptically flawed cask can ruin a future blend if not isolated before filling. Obviously physically suspect casks, with cracked bilge staves, exceedingly warped ends, worm holes or signs of previous leakage should be replaced or repaired.

It is essential that on completion of maturation, before dumping, that spirit in individual casks is nosed.

Casks require to be coded according to their origin or previous history; fresh Bourbon casks can be referred to as FB 1's (Fresh Bourbon, 1st filling). Once dumped after several years of maturation, they can be designated FB 2 casks (Fresh Bourbon, 2nd filling). Further dumpings and fillings can the casks can be coded as UR 1 or UR 2's, indicating unclassified refills, 1st or 2nd filling. Heavy, robust rums, from pot stills, would mature well in fresh Bourbon casks, while light rums would respond well to unclassified refills.

Companies are now adopting laser read bar coding identification techniques for filled casks which carry all the required information for proper inventory control.

THE AGING OF RUM—MATURATION

Noting that distillates are collected at between 80–94.0 % ABV, it is normal, unlike grain or malt whiskies to rack rums in remade American Bourbon casks at strengths of 83–85.0 % ABV. Aging, in the tropics, where the temperature remains constantly between 27–32 degrees Celsius and the relative humidity hovers between 75–90 %, is more rapid than in more temperate climates. Low humidity encourages water loss while high humidity favors alcohol loss from the cask. The high strength, which has proved to lessen maturation effects, is off set by the high temperature. Maturation losses are reputed to be in the range of 2.0 % per annum—similar to losses in more temperate climes.

Distillates with different congener compliments can be preblended before maturation. Light rums from column stills can be blended with heavy pot distilled rums prior to maturation in oak casks. Marrying mature rums for six months after blending is common.

Multiple racking may be carried out where newly blended rum is allowed to mature in cask for a few months before racking on into another cask for a further few months, this process being repeated until the desired quality is achieved. Casks for producing light rums should be such that minimum extract is produced; casks selected for this purpose will be approaching exhaustion.

Some rums, demanding long maturation periods of over ten years, may have raisins or plum wine added to them. The use of fruits or plum wine enhances the maturation effect but obviously impacts on obscuration. The majority of well aged rums possess obscurations well in excess of 1.0 %.

Warehouses tend to be of racked design, up to ten racks high, with good ventilation. Under former colonial rule, it was established that rums should like whisky, be matured for a minimum period of three years.

The definition of rum demands that it be 'a distillate produced by fermentation and distillation from sugar cane products in a sugar cane growing area, having the organoleptic characteristics normally associated with rum.'

THE AROMA AND FLAVOR OF RUM

It has been established that the great matured spirits, cognac, whisky and rum, possess common congeners, in spite of being produced from

different feed stocks. The common denominator is the impact of yeast on sugar. Each spirit carries its own signature, that special compound or combination of compounds which, when nosed impart that unique aroma, peculiar to that product, on the sense of smell (Lehtonen and Suomalainen, 1977, Nykanen and Suomalinen, 1983, de Rijke and ter Heide, 1983, Nykanen and Nykanen, 1983).

Rum is no exception. One compound has been isolated from rum—2- ethyl 3-methyl butyric acid, which is thought to emanate from bacterial action on the original molasses.

Molasses is also a haven of heterocyclic nitrogen compounds, products of the Maillard Reaction. These compounds and their relations, with exotic stereochemical shapes and names are more prevalent in rum. Although not peat derived, rum also possesses a host of phenols, some of which are fermentation derived, and others from the ethanolysis of lignin.

The unique high ester rums possess a large compliment of esters through the esterification of volatile fatty acids with ethanol. The aroma of this type of rum could almost be mistaken for fusel oil, but possesses a sweetness or fruitiness and mellowness not associated with raw higher alcohols. The ethyl esters of acetic, propionic, butyric, valeric acids and higher homologues contribute to the distinct aroma. Such rum find uses in the manufacture of flavored pipe tobaccos or is used to enhance blends of rum. Ester levels in excess of 3,800 g./LPA have been observed.

White rums and golden rums can be produced by aging for a specific time, then decolorizing with activated carbon which also will remove some of the higher esters, suppressing the original aroma. Activated carbon can only be used at alcoholic strengths less than 60.0 % ABV.

As with whisky, it is usual to reduce rums for nosing to between 20–23.0 % ABV to coax the bouquet from the liquid.

EFFLUENT DISPOSAL

As with all industries, which use water intensively, the alcoholic beverage industry is no exception, having to sewer large volumes of polluting waste streams. Rum manufacture contributes to this embarrassing environmental problem.

In firms where the environmental conscience has not been stirred; in countries where no environmental regulations are enforced or funding is low, distillery wastes can find their way into the waterways with the inevitable impact on aquatic life to the detriment of those living near the lifeless, hydrogen sulphide reeking, septic waters. The stillage is a valuable resource, containing molasses and yeast residues with a combined COD of 100,000 ppm.

It is possible to produce a syrup, very much like whisky's pot ale syrup called condensed molasses solubles. It can be further dried down to a powdered form. It is not possible to produce dark grains, but in some rum distilling areas, rice is cultivated. Rice hulls are an ideal dry cellulose source for combining with evaporated stillage to produce a potentially palatable cattle feed, thus removing two embarrassing effluent problems, one liquid, one solid, simultaneously (Murtagh, 1995).

Another route for stillage treatment is anaerobic digestion or biomethanation. One kilogram of COD can produce 0.35 cubic metres of methane. A large distillery will contribute a large COD load from which several thousand cubic metres of methane gas could be recovered weekly to generate steam, hot water and electricity.

The Bacardi Distillery in Puerto Rico has followed this route.

QUALITY

Quality can be defined as the desire to excel; consumers are becoming more educated and discerning, and will not accept inferior products.

As molasses constitutes the major cost of a rum distillery operation, it is essential that molasses is purchased at the best price, stored and handled in the most efficient manner to minimize damage to sugars and maximize their transformation into alcohol.

Yeast strains and yeast quality are of paramount importance in satisfying the rigorous fermentation requirements.

Water, sulfuric acid and ammonium sulfate are all raw materials which contribute to fermentation efficiencies, the amount and final quality of the distillates.

Good plant hygiene is an essential element in ensuring maximum yields of alcohol.

Distillation practice and the integrity of the distillation plant combine to maximize alcohol recovery as well as impacting on quality.

Cask and inventory management play their role in ensuring product quality and continuity of maturing spirit supply.

Good effluent management keeps a finger on the pulse of losses, by ensuring that good manufacturing and housekeeping practices control raw material and process waste.

Quality—Molasses

The supplier of molasses should submit an analyzes of the quality of the latest molasses which the distiller will be using. The quality of the molasses should reflect the requirements of the original agreed specification. The following parameters should be obligatory analytical requirements.

Brix/Specific gravity	Gums*
Total sugars as invert (TSAI) *	pH
Sucrose*	Color
Reducing sugars *	Odor
Sulfated ash *	Trash*
Nitrogen *	Hydroxy methyl furfuraldehyde*
Phosphate*	* values in % w/w

Total sugars can be measured by the Lane-Eynon Method, which is recognized as the standard test for sugars in molasses (Wright, 1995).

High Performance Liquid Chromatography (HPLC) is gaining acceptance for measuring the fermentable sugars—sucrose, fructose and glucose.

The specific gravity or Brix can be measured using a Brix hydrometer on a 1:1 dilution of molasses with water. The correlation between gravity and sugar content in molasses is low, because of the high concentration of unfermentable dissolved solids.

Water, Yeast and Fermentation (IoB, Methods of Analysis, 1997)

As the yeast is active dried baker's yeast, Saccharomyces cerevisiae, commanding a pivotal role in fermentation, yeast, water and fermentation performance require to be monitored microbiologically and chemically.

Quality—Water (IOB, Methods of Analyses, 1997)

The wholesomeness of water can be deduced from color, odor, microbiological and chemical characteristics.

The following microbiological checks relate to raw water supplies.

- Total Viable Count
- Isolation, identification and enumeration of Coliforms and E. coli bacteria
- Faecal streptococci
- Sulfite reducing bacteria and Clostridium perfringens

The chemical analysis of the water includes pH, conductivity, metals and salts.

Any positive count for faecal contamination however low, is unacceptable.

Where water is chlorinated, free and residual chlorine checks should be regularly carried out.

Quality—Yeast

Yeast, during propagation, is vulnerable to contamination; slurried or pressed yeasts, if not properly refrigerated, even more so, when compared with active dried yeasts whose shelf life can be extended by refrigeration. Refrigeration temperatures should be maintained between 1–5 degrees Celsius. Yeast should never be frozen.

Pitching yeasts should be regularly checked for

- Wild yeasts and bacteria
- Viability
- Haemacytometer yeast and bacterial cell count (cells/ml)—propagating medium.
- Yeast concentration by dried weight—pressed yeast

Quality—Yeast

Unpitched wash, fermenting wash and final wash are very amenable to infection. Cleanliness of plant and equipment is an essential element in controlling the growth of unwelcome contaminating organisms. The following microbiological determinations are employed to monitor for contamination.

- Total viable count of bacteria and yeasts in unpitched wash.
- Presence of spoilage organisms in fermenting wash—aerobes, lactics and wild yeasts.

Fermentation progress is monitored by regular (Six hourly) measurement of SG, (PG), pH, acidity, temperature and the alcohol content of the final wash. Residual sugars can be examined by HPLC for any unfermented sugars. Yeast viability at the beginning and end of fermentation is a good indicator of how the yeast is responding to conditions in the medium. As mentioned above, it is possible to ascertain total infecting organism levels under the same microscopic field while checking yeast viability.

Quality—Plant Hygiene

The satisfactory sanitary condition of yeast propagation, fermentation vessels and ancillary pipework are vital to the successful production of acceptable potable spirits. Adenosine triphosphate (ATP) monitoring technology has enabled hygiene checks to be carried out very rapidly for both water contamination and the cleanliness of the internal surfaces of vessels. This bioluminescence technique can be used for monitoring the effectiveness of rinsing and the overall cleanliness of recently cleaned vessels and pipework.

Quality—Distillation

The quality of final distillates is controlled by the distillation rate, the wash feed rate to continuous stills, the alcoholic strength, steam pressure, temperature and reflux rates in continuous stills; to some degree, the extent of internal surface fouling will impinge on still performance and spirit quality; sacrificial copper may be necessary to reduce the carry over of sulfur notes to the final spirit.

The presence of gums in the wash may cause foaming difficulties leading to unwelcome plate flooding and poor separation of vapor from the liquid phase.

Control is effected via the test case by hydrometry or the use of in line densitometers, coupled with regular organoleptic assessments of final spirits.

It is now possible to control continuous distillations using programmable logic controllers, linked to PC's to automatically adjust the controlling parameters, thus removing the human element, to improve quality and fuel efficiency.

In addition to the human nose, gas liquid chromatography is an invaluable tool for examining congener levels using both packed and capillary columns.

In the case of neutral spirits, the permanganate time test is still used to detect the presence of oxidizable impurities, supplementing GC analysis.

To ensure the continued quality of distillates, the following laboratory techniques are performed—

- Revenue distillations for %age alcohol in final wash.
- Pycnometry, hydrometry or densitometry to measure the per cent alcohol by volume.
- Gas chromatography to measure congener concentrations (Figs 12–7, 12–8, 12–9, 12–10). It can also be used for measuring spirit losses in stillage.
- Atomic absorption spectrometry to measure copper concentrations in lees.
- Permanganate time test for neutral spirits.
- Organoleptic assessments for acceptability or taint and off notes.

Quality—Casks

Cask quality depends on the origin of the casks to be filled. It depends on whether or not the casks being filled were derived from chooks or as free standing American barrels. The casks may be charred or uncharred.

The original oak from which the cask was made either American white oak or French.

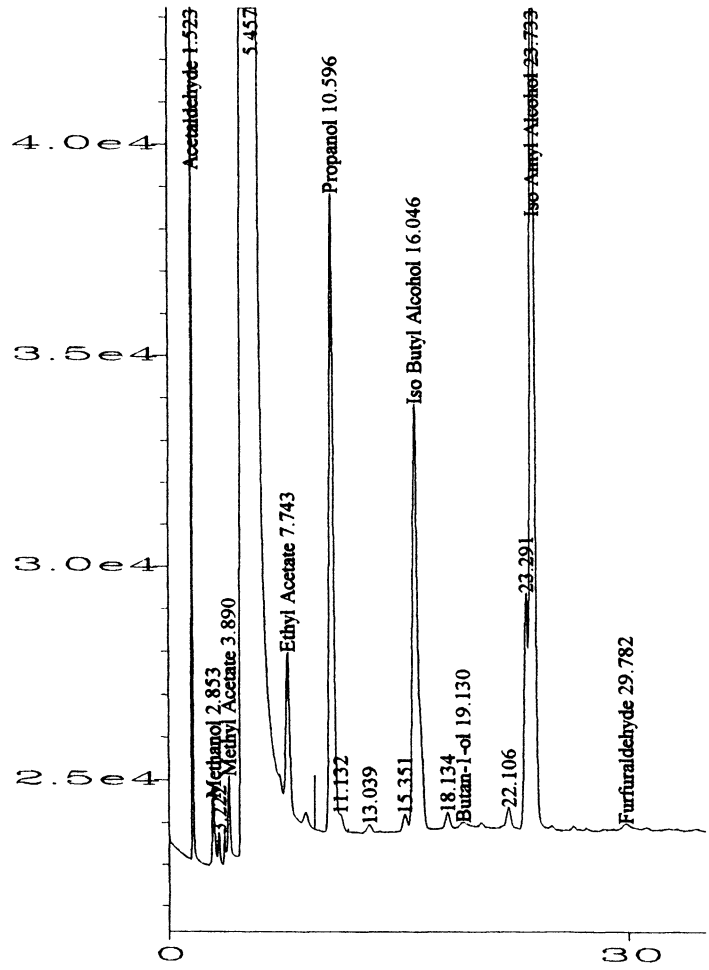


Figure 12–7 Chromatogram - Pot Distilled Rum

Limousin affects the maturation characteristics. American oak is finer grained than French oak.

The cask size also affects the maturation rate and hence spirit quality at a given age. The smaller the cask the more rapid the maturation.

Casks should be examined for physically for cracked bilge staves and badly warped ends. Worm holes, if present, can be spiled.

Sour or tainted casks should be rejected as these, if not discovered with their adverse organoleptic effects not picked up until later, could result in the unacceptable rejection of a complete batch or blend, following years of maturation.

The purchase and supply of good quality casks requires the expert eye of the cooper and is an investment which should be managed prior to filling, at filling and during maturation.

Maturation can be carried out with casks in racked or palletized warehouses.

Quality—Effluent

The control and monitoring of atmospheric emissions, aqueous discharges to water courses or sewerage works and the disposal of solid wastes is a means of reducing raw material,

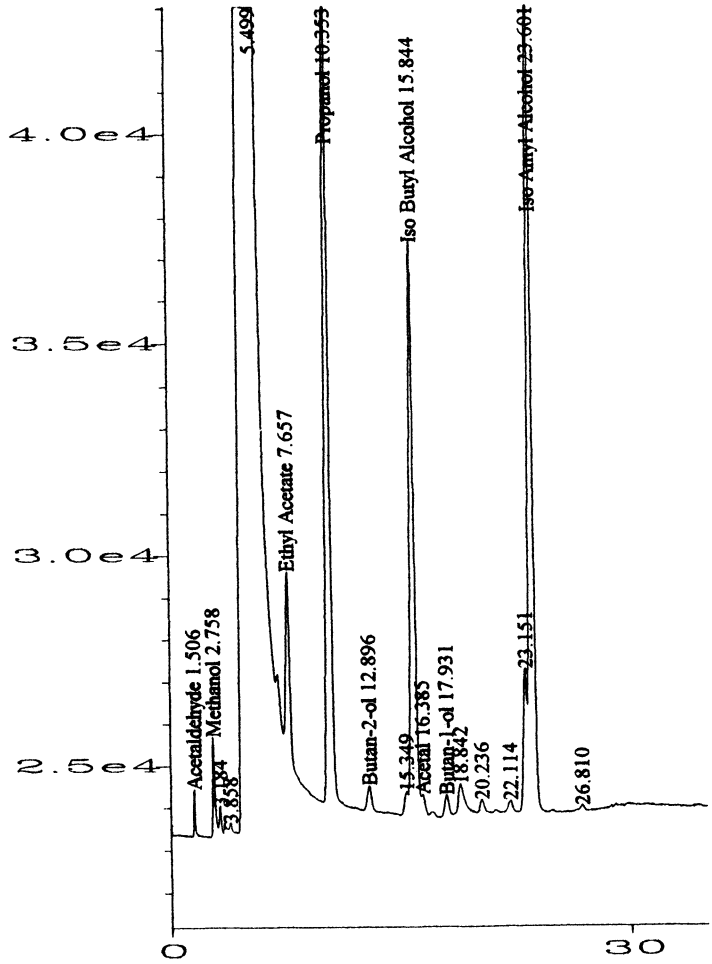


Figure 12–8 Chromatogram - Column Distilled Rum

material in progress and energy losses. The distillery can contribute to this control by monitoring boiler stack emissions to maintain high boiler efficiencies; diesel engines/generators can be finely tuned to improve fuel efficiency. Equipment is available to monitor the polluting load of aqueous discharges—BOD, COD, suspended and total solids, greases and oils. Heavy metals, like copper can be analyzed by atomic absorption spectrometry.

The maintenance of good housekeeping and manufacturing practice should be observed at all times.

Quality—Bottled Rums

As previously mentioned, the Caribbean Islands contribute more than 220 bottled rum products which excludes Demerara, in Guyana which can boast at least another dozen differ-ent rums plus a punch. The distinguishing feature across this wide spectrum of rums is their colors, from white to very dark, their ester content from less than 10 g per 100 LPA to more than 100 g per 100 LPA and obscuration which can vary from less than 1.0 % to at least 8 % depending on color and age. Higher alcohol contents will

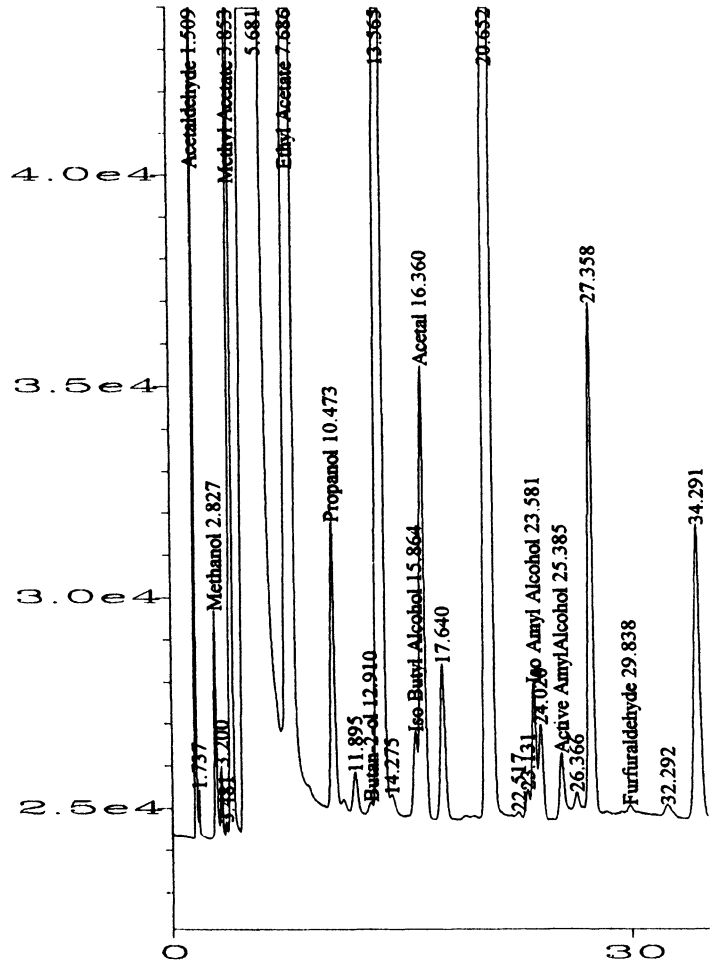


Figure 12–9 Chromatogram - High Ester Pot Distilled Rum

also vary according to the type of rum, the average being 60 g/100 LPA, which is light in comparison to some malt whiskies.

Rum has been shown to contain the largest amount of volatile fatty acids being in the order of 60 g/100LPA. Up to 90 % of the volatile acids were acetic, plus butyric and propionic acid, propionic acid being more dominant. The higher fatty acids whose esters contribute to chill haze are myristic, palmitic and palmitoleic acids (Nykanen & Nykanen,1983).

Also present in rum, in addition to alcohols, acids and esters are phenols, lactones, hydrocarbons, acetals and pyrazine derivatives.

Bottled light rums with low ester contents, low higher alcohol concentrations and little color, when originally blended, require little further treatment except reduction with demineralized water to the desired bottling strength. Chill filtration is unnecessary for local tropical markets and is not required for light rums.

The heavier rums will require chill filtration to reduce the effect of the higher fatty acid esters at bottling strength. Chilling is usually carried out at –10 degrees Celsius, much lower than Scotch whisky standards. Chilling temperature is a function of the degree of higher fatty acid ester removal required.

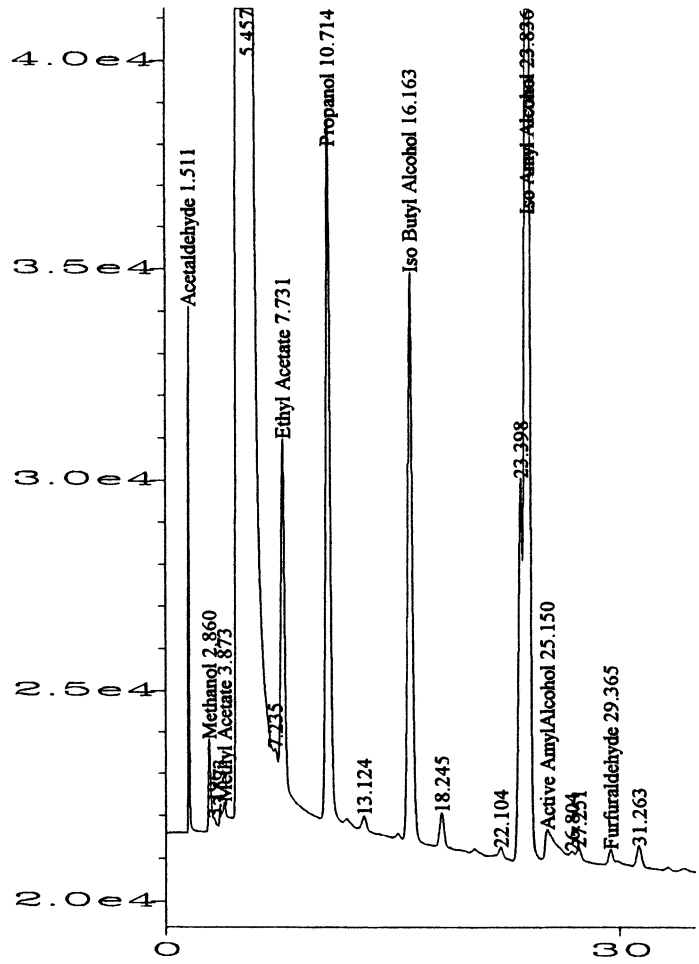


Figure 12–10 Chromatogram - 12 y.o. Mature Demerara Rum

Demineralized water for reduction usually has a conductivity of 10–15 µS.

Bottled rums are subjected to the following analytical quality checks—

1) Organoleptic
2) Alcoholic strength
3) Obscuration
4) Total acidity
5) Total sugar
6) Extract
7) Brix
8) Color
9) Turbidity
10) pH
11) Aldehydes
12) Esters by saponification
13) GC analysis (Table 12–3)
14) Metal ion analysis

Specifications are prepared with specific tolerances for each of the above parameters depending on the type of rum.

Blending and bottling vats are constructed of wood or stainless steel and filters are of the plate and frame type using coarse and sterilizing sheet filtration pads.

Table 12–3 GC Analyses of Different Types of Rum

	High Ester Rum	*Column Rum*	*Pot Rum*	*Aged Rum*
Acetaldehyde	16.2	0.6	9.5	5.8
Methanol	4.7	2.3	1.8	2.4
Ethyl acetate	96.2	–	3.9	0.9
Isobutyl alcohol	6.4	48.1	44.5	51.5
Acetal	16.5	0.6	–	–
Isoamyl alcohol	4.7	31.5	47.9	75.4
o.a. Amyl alcohol	2.7	–	–	3.1
Furfural	0.8	–	0.7	1.2

Results expressed in g / 100 litres A. A.

CD Column: glas 2m., O.D: 0.25 inch, I.D: 2.0 mm, Phase A: 5.0% Carbowax 20M, Mesh Size : 80/120, Support : Carbopack BAW Chromatograph : H-P 5890, Temperature : 70 degrees Celsius, isothermal

At each prebottling stage the product to be bottled is checked against quality parameters, the final bottling vat attracting the most attention.

SUMMARY AND CONCLUSION

The islands of the Caribbean, Puerto Rico, Dominica, US Virgin Islands, British Virgin Islands, Martinique, Saint Lucia, Saint Martin, Sint Maarten, Saint Vincent, Cartiacou, Antigua, Grenada, Saint Kitts, Barbados, Guadeloupe, Trinidad, and Marie Galante, sound like a roll call of West Indian holiday destinations. With Demerara on the continent of South America, they contribute over 230 bottled rum products to the consumer market.

From the early days of the sugar estates, dependent on slave labor, the products, both bottled and bulk, in cask or larger container, found their way to the four corners of the earth as bulk exports for maturation in the USA, Canada or Europe or as famous bottled products, produced and bottled in the Caribbean.

So varied are the individual rums that they can be used as mixers or like cognac or fine malt whiskies, as post prandial drinks to savor after a good meal.

Blenders of rum can reflect on its nautical past with some apprehension when pirates were ambassadors of the drink, while Churchill's famous dictum that the British Navy ran on 'Rum, sodomy and the lash', sends shivers down the spine (The Rum Information Bureau).

It was Admiral Penn, who first issued rum to sailors, sweetened with limes, in 1655. In 1731, the Navy Board introduced a daily ration of half a pint per rating. Between 1731 and 1740, so many sailors had plunged to their deaths from the rigging of ships, that in 1740, Admiral Vernon, noted for wearing a coat of grogram, commanded that the rum be issued 50:50 diluted with water. Thus a mixture of rum and water was henceforth known as 'grog.'

Admiral Nelson, following his death, at the Battle of Trafalgar was transported to England in a container of rum. On the return, a shortage of rum ensued and one or two tars helped themselves to a tot from the cask, which obviously contained droplets of Nelson's blood. Thus rum also earned the appellation, 'Nelson's Blood'.

In 1970, the Admiralty Board abolished the daily ration.

From the blood and sweat of the early slaves, stretching back three hundred and fifty years, to the abolition of slavery and the emancipation of the slaves in the former colonies, just over one hundred and sixty years ago, rum continues to be perfected by freemen, descendants of the original slaves and by East Indians to the present day.

Modern equipment and techniques are replacing some of the age old traditions but the quality of the product remains superb.

Rum, like whisky, cognac and armagnac, can be deemed to be a noble spirit in the tradition of cask matured products.

As long as the world continues to demand cane sugar, rum will continue to be distilled wherever the cane is grown.

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13

Vodka, Gin and Other Flavored Spirits

R. I. Aylott

INTRODUCTION

Vodka, gin and the broad category of flavored spirits normally use high-purity alcohol as their base. They may then subject to further processing to give their required flavor characteristics. Products in this category are normally colorless and are not subject to maturation processes, as are whisky, brandy and rum. Their alcohol base is typically neutral alcohol (otherwise known as ethyl alcohol of agricultural origin), a highly rectified material distilled at > 96 % v/v alcoholic strength. Vodka is simply based on pure alcohol, although some vodka is flavored. Gin is based on alcohol distilled or flavored with juniper and other botanical materials. Other European spirits are flavored with juniper and include genever and steinhager. Other spirits take their flavor from caraway (aquavit), aniseed (anis, pastis and ouzo) and bitters. Flavored spirits may be described as one category within the spirits industry as a whole (Watson, 1993). Two recent books useful for background reading include Classic Vodka (Faith and Wisniewski) and Classic Gin (Coates).

Vodka, gin and flavored spirits are mostly sold at between 35 and 40 % v/v alcoholic strength (depending on local regulations for minimum alcoholic strengths), although strengths up to 47.3 % are often found in duty-free markets. These products may be drunk neat, with other alcoholic beverages in cocktails or with non-alcoholic mixer drinks (such as tonic and soda) according to taste. Vodka, gin and anis/pastis are the major products in the flavored spirits' category in terms of their worldwide production volumes and, therefore, form the principal subjects of this review.

Vodka

Vodka is a pure unaged spirit distilled from various materials and normally filtered through charcoal. Vodka originated in Poland and Russia and is integral to the social life of these countries. The product dates back many hundreds of years, probably to the twelfth or thirteenth centuries. Finland and Sweden are also major producers. Vodka's popularity in western countries increased considerably in the second half of the twentieth century. It is now produced in many countries throughout the world, although many of the most popular brand names have Eastern

European connotations. Vodkas may also be flavored using a variety of materials such as orange and lemon peels, ginger, cloves, peppers, blackcurrant and sugar.

Gin

Gin is made by flavoring alcohol with appropriate botanical substances. The key ingredients are high-quality neutral alcohols, botanical substances such as juniper, coriander and angelica and pure water. 'Distilled gin' is made by distilling neutral alcohol and water in the presence of botanical materials, diluting this product further with alcohol according to local definition and reducing with water down to bottling strength. The term 'London dry gin' is a type of distilled gin that may be produced anywhere, whereas 'Plymouth gin' reflects geographical origin.

Gin originated in Holland and was brought to England in the late sixteenth century by soldiers returning from fighting in the Low Countries. The name gin is a corruption of genievre, the French word for juniper. Gin soon began to compete with the two other spirit drinks in England at that time, namely rum from the West Indies and brandy from France. In 1688 William of Orange became King of England and passed an Act banning the import of foreign spirits, an action designed to support English grain farmers by encouraging the distillation of gin from home-grown grain.

The useful book entitled The World Guide to Spirits quotes gin consumption increasing from half a million gallons in 1690, to nearly 5 million gallons in 1727 and reaching 11 million gallons production in London alone by 1733 (Lord, 1979). The consequent drunkenness and disorder resulted in the 1736 Gin acts, which were designed to reduce the number of gin shops and increase its price. The Act failed in its purpose and was repealed in 1743, at which time production had reached 20 million gallons. A more reasonable Act was introduced in 1751. Gin in this period was pungent, no doubt because of the limited rectification of its alcohol base in the copper pot stills of the period, thus being relatively rich in fermentation congeners compared to modern neutral alcohol. This gin was usually flavored with lemon or sweetened with sugar (the latter being known as Old Tom). In the second half of the nineteenth century unsweetened or 'dry' gin appeared and this is thought to be more similar to the popular gin of today, known as 'London dry gin'.

Other Flavored Spirits

A wide variety of other flavored spirits are produced throughout the world, the most famous category being anis, pastis and ouzo. Anis and pastis have their origins in absinthe, a drink created in the late eighteenth century in France using a mixture of herbs including wormwood. Absinthe became very popular in France; however, it was subject to abuse through over consumption and was considered to contain potentially dangerous components. This resulted in a French government ban on its manufacture in 1915 during the First World War.

Pastis (meaning mixture) is made using wormwood and anise. Pastis was also banned in France during the First World War, after which Paul Ricard introduced his now famous brand. It was banned again during the Second World War but has since grown to be a major global brand. Both anis and pastis are colored, unlike most gins and vodkas. On diluting with water, anis goes from yellow to greenish yellow and pastis goes from brown yellow to a grey color.

The other famous aniseed-flavored spirit is ouzo from Greece. Similar products, such as aguadiente come in South America where cane alcohol is flavored with an anise extract and sweetened. Other spirits are based upon flavoring by caraway (aquavit) and bitters.

DEFINITIONS AND REGULATIONS

Vodka and gin, together with other major spirits drinks are defined in the European Union spirit drinks regulations (Council Regulation (EC) No. 1576/89, 1989). Similar regulations exist in the USA (Code of Federal Regulations, 1991),

Canada (Canada Gazette, 1993) and Australia (Commonwealth of Australia Gazette, 1987) and these are reviewed in this section. Many other countries have parallel regulations, which often reflect the definition in the product's country of origin.

Neutral Alcohol

Most regulations only permit the use of ethyl alcohol of agricultural origin, that is alcohol fermented from a carbohydrate source. This obviously precludes the use of synthetic alcohol produced from fossil fuels. Annex I of the European Union regulations, summarized in Table 13–1, defines ethyl alcohol of agricultural origin in terms of its organoleptic characteristics, minimum alcoholic strength at 96.0 v/v and maximum level of residues (Council Regulation (EC) No. 1576/89, 1989). The minimum strength for neutral spirit in the USA is 95 % v/v (190 ° US proof). However, most good quality neutral alcohols significantly exceed these minimum purity standards.

Vodka

Vodka is defined in the European Union spirit regulations as 'a spirit drink produced by either rectifying ethyl alcohol of agricultural origin or filtering it through activated charcoal . . . so that the organoleptic characteristics of the raw materials are selectively reduced'. Additional flavorings are permitted to give special organoleptic characteristics such as a mellow taste.

The United States BATF regulations define vodka as 'neutral spirits so distilled, or so treated after distillation with charcoal or other materials, as to be without distinctive character, aroma, taste or color'. The minimum bottling strength is 40 % v/v and additives are permitted (which include sugar at < 2 g/l and citric acid at < 150 mg/l). United States regulations have a separate definition for flavored vodka, which includes a minimum bottling strength of 35 % v/v. The Canadian regulations define vodka as 'a potable alcoholic beverage obtained by the treatment of grain spirit or potato spirit with charcoal so as to render the product without distinctive character, aroma or taste. Additives are not permitted. Australian vodka regulations follow the same pattern as gin permitting certain additives and having a minimum bottling strength of 37 % v/v.

Gin

The European Union regulations for gin are perhaps the most comprehensive. A drink may be called gin if it is produced by flavoring organo-

Table 13–1 Characteristics of ethyl alcohol of agricultural origin (Council Regulation (EC) No.1576/89, 1989)

Organoleptic characteristics	*No discernible taste other than that of the raw material*
Minimum alcoholic strength by volume	96.0 % vol.
Maximum level of residues (measured as g/100 litres alcohol at 100 % vol.)	
Acidity: acetic acid	1.5
Esters: ethyl acetate	1.3
Aldehydes: acetaldehyde	0.5
Higher alcohols: 2-methyl 1-propanol	0.5
Methanol	50
Dry extract	1.5
Volatile nitrogen bases: nitrogen	0.1
Furfural	Not detectable

leptically acceptable ethyl alcohol of agricultural origin with natural and/or nature-identical flavoring substances so that the taste is predominantly of juniper. Distilled gin is further defined as being 'produced solely by redistilling suitable ethyl alcohol of agricultural origin of an appropriate quality with an initial alcoholic strength of 96 % vol. in stills traditionally used for gin, in the presence of juniper and other natural botanicals provided that the juniper taste is predominant'. The term also applies to mixtures of distilled gin and ethyl alcohol and natural and/or nature-identical substances may also be used. Gin made simply by adding essences or flavorings to ethyl alcohol may not be called distilled gin and is referred to here as a compounded gin. The minimum alcoholic strength for release for human consumption in the European Union is 37.5 % v/v. Minor regulations also apply to gin in certain member countries. For example, the maximum permitted lead concentration in gin (and other spirits) in the UK is 0.2 ppm (Dukes, 1984)—not that this compound is detectable in modern gin.

The United States Bureau of Alcohol, Tobacco and Firearms (BATF) regulations differ from those of the European Union in two main respects. First, distilled gin must be produced by original distillation or redistillation. Secondly, gin may not be bottled at less than 80 US proof (40 % g/g). The Canadian regulations do not use the term distilled gin and have a minimum alcoholic strength of 40 % v/v. Australian regulations permit gin to contain sugar, honey and flavorings, stipulate a maximum methanol concentrations of 0.4 g/l ethanol and have a minimum bottling strength of 37 % v/v.

Other Flavored Spirits

European Union regulations for other flavored spirits tend to be quite precise, depending on the product in question. Products based on the use of ethyl alcohol of agricultural origin include gentian spirits, fruit spirit drinks, juniper-flavored spirits other than gin, caraway-flavored spirit drinks and aniseed-flavored spirit drinks.

A range of juniper-flavored spirits other than gin are described, although the taste of juniper berries need not be discernible. These include genievre, jenever, genever and pecket. Caraway- and aniseed-flavored and bitter-tasting drinks are specifically defined and include details of the botanical ingredients, their maceration and/or distillation processes, distillation strengths and proportions of distillate in final product, sugar and anethole concentration ranges and dry extract values.

Aniseed-flavored spirits include anis, pastis and ouzo. Anis must derive its characteristic flavor from combinations of anise, star anise and fennel. Pastis must also contain natural extracts of liquorice root and have a maximum sugar concentration of 100 g/l and an anethole concentration between 1.5 and 2 g/l. Ouzo must be made in Greece, be colorless and have a maximum sugar content of 50 g/l (amongst other detail). These regulations are in part summarized in Table 13–2 and the reader is referred to the Official Journal for detailed information (Council Regulation (EC) No. 1576/89, 1989).

In recent years, a number of governments have sought to avoid or minimize the use of certain botanical materials on the grounds that they contain compounds about which there is toxicological concern. Although there is no concern over the botanical materials used to flavor the major flavored spirits, it is a subject about which spirit manufacturers must be aware. European Union regulations lay down definitions of flavorings for use in foodstuffs (Council Directive of 22 June, 1988). This 1988 Directive also applies to alcoholic beverages and defines maximum limits for certain substances obtained from flavorings, which include coumarin, hydrocyanic acid, safrole and thuyone. It also requires the Commission to create inventories of flavorings and flavoring source materials. This activity has led to a proposal for a Community procedure for flavoring substances used in foodstuffs (Commission Proposal, 1994).

Canada has proposed an amendment to its Food and Drug Regulations concerning herbs and botanical preparations sold as food (Canada

Table 13–2 Major flavored spirits defined within European Union regulations (Council Regulation (EC) No. 1576/89, 1989)

Predominant taste	*Botanical name*	*Product names*	*Minimum alcoholic strength (% v/v)*
Juniper	*Juniperus communis*	Wacholder, ginebra, genebra, genievre, jenever, genever, peket gin, distilled gin	37.5
Caraway/dill	*Carum carvi* L./ *Anethum graveolens* L.	Akvatit, aquavit	37.5
Aniseed			
Star anise	*Illicium verum*	Anis	35
Anise	*Pimpinella anisum*		
Fennel	*Foeniculum vulgare*		
Aniseed + liquorice	*Glycyrrhize glabra*	Pastis	40[a]
Aniseed + mastic	*Pistacia lentiscus* Chia	Ouzo	37.5[b]
Bitter		Amer, bitter	15
None		Vodka	37.5
Mellow taste		Vodka	37.5

[a]Plus sugar at < 100 g/l.
[b]Plus sugar aPt < 50 g/l

Gazette, 1992). However, the amendment notes that a number of preparations that will be classed as adulterants can safely be used as flavorants in alcoholic beverages provided the biologically active component is not present in the finished product. Australia has also proposed prohibiting the use of certain plants (or parts thereof) on the basis that these items pose an unacceptable risk to public health and safety (National Food Authority, 1993).

BRANDS, MARKETS AND VOLUMES

Vodka

World-wide sales figures for vodka are more difficult to quantify than those for gin because of the markets in which it is dominant. Total sales were estimated at 60 million cases in 1990 and growing by about 1 % per year. This total excludes figures for the former Eastern Bloc, which probably sells at least three times this figure. The major vodka markets (excluding the former Eastern bloc) are the USA (60 %) and the UK (6 %). Other significant markets include Sweden, Finland, Germany, Canada, South Africa and Brazil. Vodka production in Russia is estimated at around 1500 million litres (International Drinks Bulletin, 1993).

Vodka was represented by 17 of the World's top 120 spirit brands in 1999 with sales of these brands alone exceeding 120 million cases (Drinks International). Full details are given in Table 13–3. Stolichnaya vodka from Russia was the most popular brand selling 53 million cases and with exports exceeding 10 % was categorized as an international brand for the first time. Smirnoff Vodka was third after Bacardi Rum international brand and sixth in overall popularity. Other major international brands include Absolut Vodka (from Sweden), Wybororwa (from Poland) and Finlandia (from Finland). There are 108 brands of vodka listed in the trade press. The major brands in the UK on-trade in 1992 were Smirnoff, Vladivar, Zamoyski, Cossack and Imperial (with a combined 87.9 % market share) and the off-trade equivalents were Smirnoff, Vladivar, Grant's, Checkov and Stolichnaya (with

Table 13–3 Vodka brands amongst the top 120 spirit brands World-wide (Sales, millions of nine litre cases)

Rank	*Vodka brand*	*Brand owner*	*1997*	*1998*	*1999*	*Key markets*
1	Stolichnaya	Solutzplodimport	52.0	52.8	53.2	International/Russia
6	Smirnoff	Diageo	15.5	15.9	16.3	International
7	Moskovskaya	Solutzplodimport	13.6	13.8	14.0	Russia
11	Absolut	Absolut/Vin & Sprit AB	5.5	5.9	6.4	International
17	Zytmia	Agros/Polmos	6.0	5.0	5.3	Poland
20	Wyborowa	Agros/Polmos	6.0	5.5	5.0	International/Poland
23	Absolwent	Polmos Bialystok	0.4	3.7	4.0	Poland
43	Lodawa	Polmos/Poznan	2.5	3.2	2.8	Poland
55	Popov	Diageo	2.7	2.3	2.2	USA
56	Krakus	Agros/Polmos	2.8	2.3	2.2	Poland
63	Gordons	Diageo	2.2	2.2	2.0	USA
75	Finlandia	Primalco	1.6	1.7	1.7	International
81	McCormick	McCormick Distilling	1.3	1.4	1.5	USA
86	Korsenkova	Primalco	1.5	1.4	1.3	Finland
87	Barton	Canandaigua/Barton	1.3	1.3	1.3	USA
104	Premium	Polmos/Poznan	2.0	1.2	1.1	Poland
110	Kamchatka	JBB Worldwide	1.1	1.1	1.1	USA
114	Skol	Canandaigua	0.9	1.0	1.0	USA

Drinks International, Wilmington Publishing Ltd., London, April 2000, 47–64.

a combined 47.5 % market share) (The Drink Pocket Book, 1994). The major brands in Russia are Stolichnaya, Moskovskaya, Pshyenechnaya, Siberskaya and Limmonaya.

Gin

World-wide sales of gin were estimated at 30 million cases (9 litre) in 1991 and were reducing at about 2 % per year. The major markets are the USA (40 %), Spain (22 %), UK (11 %) and South Africa (3 %). UK gin production in 1992 was over 38 million litres pure alcohol (lpa), of which over 9 million lpa was exported into the European Community and 15 million litres was exported elsewhere. Most UK exports go to the USA, Spain, France, Germany and Canada (Wilkinson, 1993). Although UK is a major net exporter of gin, this amounts to less than 10 % of Scotch whisky exports (The Drink Pocket Book, 1994).

Gin is represented in seven of the World's top 120 spirit brands by San Miguel, Gordon's Seagram's, Larios, Beefeater, Gilbey's, and Tanqueray gins (Drinks International). Full details are given in Table 13–4. There are 109 brands of gin listed in the trade press (Wine and Spirit International Yearbook, 1993). Gordon's, Beefeater, Gilbey's and Tanqueray gins are international brands, whereas San Miguel, Seagrams and Larios gins have strong regional markets in the Philippines, USA and Spain, respectively. The major brands in the UK on-trade during 1992 were Gordon's, Beefeater, Gilbey's, White Satin and Booth's (with a total 93.5 % market share) and the off-trade equivalents were Gordon's, White Satin, Beefeater, High and Dry, and Gilbey's (with a total 52.3 % market share) (The Drink Pocket Book, 1993). This information demonstrates the varying strength of specific brands in the different market sectors of various countries.

Other Flavored Spirits

Drinks in the anis/pastis category appear at number nine and 53 of the World's top 120 spirit

Table 13–4 Gin brands amongst the top 120 spirit brands World-wide (Sales, millions of nine litre cases)

Rank	*Gin brand*	*Brand owner*	*1997*	*1998*	*1999*	*Key markets*
4	Ginebra San Miguel	La Tondena	26.2	22.8	25.5	Philippines
15	Gordon's	Diageo	5.4	5.4	5.4	International
26	Seagram's	The Seagram Co.	4.0	3.8	3.6	USA
42	Larios	Pernod Ricard	2.7	2.8	2.9	Spain
59	Beefeater	Allied Domeq	2.1	2.2	2.2	International
60	Gilbey's	Diageo	2.5	2.3	2.2	International
71	Tanqueray	Diageo	1.6	1.6	1.8	International

Drinks International, Wilmington Publishing Ltd., London, April 2000, 47–64.

brands in 1999 with Ricard and Pastis 51 (both sold by Pernod Ricard). These products sold 7.5 and 2.3 million cases, respectively, in 1999. Aguardiente (cane neutral alcohol) is flavored with anise and sugar in Latin America, particularly Colombia, where it sells relatively cheaply in very large volumes.

Next in popularity appear Fernet Branca bitter/aperitif (ranked 65), Fernet Stock bitters (70), Suze bitter/aperitif (101), Aalborg Akvavit aquavit (111), Cynar bitter/aperitif (120), each selling between one and two million cases (International Drinks Bulletin, 1999).

Elsewhere, there are many and diverse regional brands of flavored spirits. For example, Cachaca is continuously distilled from sugar cane in Brazil; however, it can be rich in congeners and its distinct character is less neutral than other products in this category. One cachaca brand, Pirassanunga 52 (ranked third in volume globally) sold 26 million cases in 1999. Brazil also produced flavored spirits known as conhaques (fitting a local definition of brandy). Products such as Dreher and Presidente are based on cane alcohol and flavorings. Some countries, particularly India, have local brands based on local extra neutral cane alcohol (known as ENA) plus flavorings (some of which are based on traditional whisky). These flavored spirits are given the local designations of whisky, brandy and rum and are known as "Indian made foreign liquors" (IMFL). It is important to note that IMFL descriptions are not accepted in the regulations of most countries outside India. Indian whisky brands such as Bagpiper, McDowell's No. 1, Directors Special, Kerala Malted and Officer's Choice each sell between 2 and 3 million cases (Drinks International, 2000).

VODKA, GIN AND FLAVORED SPIRIT PRODUCTION

Neutral Alcohol

Neutral alcohol is the common ingredient in the manufacture of flavored spirits described in this chapter. The neutral alcohol production process varies according to the carbohydrate source, although the key stages are cooking, mashing, fermentation and distillation. The production of alcohol for use in the manufacture of flavored spirits is a separate operation from any subsequent botanical distilling or compounding operation and is normally undertaken at a different location and often by a different company.

As mentioned above, the chemical characteristics of ethyl alcohol of agricultural origin are defined in Annex 1 of the 1989 European Union spirit regulations (Table 13–1). Alcohol to be used in flavored spirit manufacture normally achieves much lower levels of residual congeners than the regulated maxima. For example, grain and molasses alcohols have much lower methanol concentrations than the maximum permitted 50 g/100 litres absolute alcohol. Neutral alcohols derived from wine-spirit tend to have higher methanol concentrations, which may be

reduced by using high rectification distillation systems. The reader is referred to Simpson (1977, 1984) and Clutton (1979) for further information.

Neutral alcohol fermented from cereals (such as maize and wheat) first requires the starch to be gelatinized. This can be achieved by milling and steeping or by cooking. Cooking is achieved under elevated pressures (typically 2.5–4 atmospheres) and at high temperatures (135–150 °C) in either batch or continuous cookers. Batch cooking takes about 3 hours but continuous cooking at higher pressures takes less than 1 hour. About 1 % malted barley may be added to partially liquefy the starch and improve handling characteristics (Clutton, 1979). As there is no requirement for grain neutral alcohol to be produced from the whole grains of cereals (as is the case for whisky), the opportunity exists for the distiller to recover bran and protein from the grain before mashing. These by-products may be produced in a joint venture operation with a partner who can make direct use of the by-product. Mashing, the conversion of starch into dextrins and then fermentable sugars, takes place with either natural malt enzymes or manufactured enzymes (Godfrey, 1979). The resulting wort is now ready for fermentation. When beet or cane molasses are used as the carbohydrate source, the above procedures are unnecessary as the carbohydrate is in a readily fermentable form.

Fermentation by the addition of yeast to the wort (using specific strains of *Saccharomyces cerevisiae* at approximately 0.1 %) takes about 40 hours and produces an alcohol content in the range 6–10 %. Distillers' yeasts are normally supplied by a specialized yeast manufacturer. It is common for the carbon dioxide evolved during fermentation to be collected as a by-product for sale in gaseous, liquid or solid forms.

Alcohol in the fermented wash is then purified and concentrated using continuous distillation on at least two and up to five columns. The first column, known as the wash or beer column, separates the alcohol from the fermented wash. Preheated wash enters the top of the column and is met by steam from the bottom. Alcohol and other vapors rise to the top of the column while spent wash runs down to the bottom and is led off to a by-products plant for recovery of spent grains. Spent wash is rich in protein and oils and is recovered for subsequent use in animal feedstuffs. The second column is the rectifier and concentrates the alcohol to a higher strength at the spirit take-off point near its top.

Most neutral stills utilize a third purifier column between the wash columns and final rectifier, applying a technique known as hydroselection or extractive distillation. Wash column distillate enters about halfway up the extractive distillation column and water, maybe up to 20 times as much, is fed in at the top. The addition of water alters the relative volatilities of the components in the wash column distillate. This enables the removal of remaining esters, aldehydes and other trace congeners—concentrating towards the top of the column. The majority of ethanol is removed with the majority of water from the bottom of the column. A final rectification will bring the ethanol up to strength and recover water. Distillation columns are typically 20–40 m high and are constructed from stainless steel, often with copper sections or inserts to improve spirit character.

Vodka

Vodka production simply requires high-purity alcohol so that its character comes from the ethanol. The alcohol is normally distilled from a grain fermentation, although potatoes may be used as the carbohydrate source in Poland and Russia, beet and molasses are often used in Western countries and cane in Latin America, Africa, India and the Far East.

Vodka spirit is normally subjected to further processing with activated carbon in order to reduce the concentrations of trace congeneric materials, which may impart sensory character. This may be achieved by either dispersing and agitating powdered charcoal in a large volume of spirit followed by its removal by filtration, or by passing the spirit down one or more columns packed with granular charcoal onto which trace congeners are adsorbed. The quality parameters

applicable to the alcohol and water required for vodka production are similar to those discussed earlier for gin.

Some vodka brands are reduced to packaging strength simply with pure water, filtered and bottled. Others have added trace additives such as sugars, glycerol, propylene glycol or other flavors in order to impart a smooth mouth-feel and also to give a residue on analysis in markets where simple alcohol-water combinations are not permitted by regulation (Table 13–6).

Gin

The two methods of gin production involve distillation with or without subsequent compounding and simple compounding. "Distilled gins" are made by distilling neutral alcohol and water in a traditional gin still in the presence of juniper berries and other botanical ingredients. The resulting distillate may be simply reduced with water prior to bottling or a strong flavor distillate may be compounded with neutral alcohol, and then reduced with water. Compounded gins (which may not be designated as distilled gin) are simply mixtures of neutral alcohol, juniper-based flavors or essences and water. Distilled gins are generally considered of premium quality. Gin is now distilled in many countries including the UK, USA and Spain. Gin compounding and bottling takes place in these and many more countries according to local demand. The reader is referred to a number of useful articles by specialists in the industry (Simpson, 1966, 1977; Wilson, 1976; Clutton, 1979; Rogers, 1993).

Materials for Gin Production

The three key ingredients in gin manufacture are botanical materials, neutral alcohol and water, each of which must meet exacting quality standards. The essential botanical ingredient is the juniper berry (*Juniperus communis*), which is commonly harvested in Italy and former Yugoslavia. The second commonly used ingredient is coriander seed (*Coriandrum sativum*) typically from Morocco and Russia, followed by angelica (*Archangelica officinalis*) from central Europe and orange and lemon peels. The precise

Table 13–5 Typical botanical materials selected for gin distillation

Common name	*Botanical name*	*Principal origins*
Juniper berries	*Juniperus communis*	Italy, Central Europe
Coriander seed	*Coriandrum sativum*	Morocco, Eastern Europe
Angelica root	*Archangelica officinalis*	Germany
Sweet orange peel	*Citrus sinensis*	Italy
Bitter orange peel	*Citrus aurantium*	Spain
Lemon peel	*Citrus limon*	Mediterranean
Aniseed	*Pimpinella anisum*	Mediterranean, China
Calamus root	*Acorus calumus*	
Caraway seed	*Carum carvi*	Holland, Eastern Europe
Cassia bark	*Cinnamomum cassia*	Vietnam, Ceylon
Cardamom seeds	*Elettaria cardamomum*	India, Central America
Cinnamon	*Cinnamomum zeylanicum*	Sri Lanka
Fennel seed	*Foeniculum vulgare*	Mediterranean, temperate regions
Grains of paradise	*Afromomum melegueta*	Ghana
Liquorice root	*Glycyrrhiza spp.*	
Nutmeg	*Myristica fragrans*	East and West Indies
Orris root	*Iris pallida*	
Savory herbs	*Satureja hortensis*	France, Mediterranean

From Simpson (1977), Clutton (1979), Heath (1981), Rogers (1993).

recipes used in particular brands are closely guarded commercial secrets. However, use of juniper berries, coriander seeds, cinnamon bark, angelica root, lemon peel and cardomom have been reported (Wilkie et al., 1937). Some manufacturers are less secretive. For example, Bombay Sapphire Gin has juniper, coriander, angelica, cassia bark, cubeb berries, orris, liquorice, almonds, lemon peel and grains of paradise listed on its bottle label. Table 13–5 lists commonly used botanical ingredients.

The gin distiller requires botanical materials of both a high and consistent quality. This means that a distiller will assess the moisture and oil content of parcels of botanical materials, as well as their sensory properties. As the moisture content of juniper berries diminishes during storage, slight changes in their sensory character also occur and this is taken into account when blending botanicals prior to distillation (Rogers, 1993).

Alcohol for gin distillation must be neutral, having no distinctive character, aroma or taste so that all the gin flavor comes from the botanical ingredients. Individual distillers will have their own specifications for alcohol, both in terms of sensory character and chemical purity. In particular, distillers require alcohol to be free of any trace congeners, which may impart a sensory character. The alcohol may be fermented from a number of carbohydrate sources including grain (maize or wheat), molasses, grapes, potatoes and lactose (from whey). Gin distilled from grain is often presented as the premium quality, but it is possible to obtain excellent alcohol from other substrates providing there is appropriate rectification during distillation. The choice of carbohydrate source depends upon quality, availability, branding, price and any local tariff restrictions in the country of manufacture.

Water for both gin distillation and strength reduction prior to bottling must be clear, pure and without any odor or taste. Historically, distilleries were located near good sources of water (such as Clerkenwell and Goswell near the City of London). However, nowadays good quality water may be obtained from most local supplies when treated by an appropriate demineralization process at the distillery/bottling plant. The demineralizing plant normally includes deionization (by ion exchange) followed by carbon filtration and UV irradiation to eliminate any microbiological activity in the water. Demineralized water is normally subjected to both sensory and chemical quality checks. A sample representative of the bulk liquid will be nosed to ensure the absence of any foreign odors. pH and conductivity will be checked to ensure that the demineralizing plant is working within specification.

Gin Distillation

Gin distilling is a traditional batch process using copper pot stills similar in shape to those used for Scotch malt whisky. Their design has remained the same over many generations and is specific to a particular brand. Gin stills were originally directly fired, although this has now been replaced by steam heating. Stills have long lives because the ingredients of gin distillation pro-

Table 13–6 Analytical profiles of six different brands of vodka components of which may be used to support brand authenticity analyses.

	Brand 1	*Brand 2*	*Brand 3*	*Brand 4*	*Brand 5*	*Brand 6*
Alcoholic strength, % v/v	40.0	37.5	37.5	37.5	37.8	37.6
Additive, mg/litre						
Propylene glycol	ND	ND	ND	ND	ND	47
Glycerol	ND	ND	80	ND	ND	ND
Glucose	ND	1570	ND	29	ND	ND
Fructose	ND	1370	ND	27	ND	ND
Sucrose	ND	3	ND	39	2200	ND

ND = Not detected

duce a neutral pH environment, compared to the more acidic conditions of malt fermentation. Two generations of gin distillery, shown in Figure 13–1, illustrate the traditional nature of distilled gin production (Kinross, 1959; Wilson, 1976).

The botanical ingredients, the quantities used and the method of their distillation are specific to each brand of gin. The process begins with the still being charged with water and then alcohol added to give a mixture at the desired alcoholic strength for distilling. The volume of this charge may be typically 50001 at a strength of around 60 % v/v. The botanical ingredients are then added to the still, either loose or in a bag (which may be suspended in the headspace above the liquid). The still is then closed and heat applied through steam coils in the bottom of the still. As the liquid heats up, some of the more volatile of the botanical congeners start to boil and are distilled with ethanol. The rate of heating is carefully controlled by steam regulation and the alcoholic strength of the distillate is monitored using a hydrometer located in the spirit safe below the still condensers. This first part of the distillate is known as the heads and is not required. It is therefore collected separately from the main gin fraction. The next and main fraction is collected as gin product at around 80 % v/v strength. Towards the end of this batch distillation, the alcoholic strength of the distillate drops and the character of the distillate changes as the less volatile of the botanical congeners start to dominate the character of the distillate. This third or tails fraction is then collected using maximum heating in order to recover the remaining alcohol in the still. The heads and tails fractions are then combined as feints and purified in a separate distillation at the gin distillery or returned to the alcohol industry for recovery of neutral alcohol.

The gin fraction is subjected to rigorous sensory checks. Before being transferred from the distilling to the bottling operation, it may be blended with other gin distillates and alcohol in order to produce the final gin. This product is normally at a relatively high alcoholic strength and reduction with water is required to bring the gin down to bottling strength.

Compounded Gin Production

The simplest method of gin manufacture involves adding essences or flavorings to ethyl alcohol. Essences are normally manufactured separately by an independent flavor company and sold to a gin bottler who may combine various essences and then compound these with alcohol before reduction to bottling strength. Natural essences may be produced by steam or alcohol distillation of botanical materials. In addition, nature-identical compounds may be used by essence manufacturers, if allowed by local regulations, in order to achieve specific sensory characteristics. Such products may not be called distilled gin.

Flavored Gins

There are a number of speciality products which are based on gin for both flavor and alcohol contribution. These include sloe, orange and lemon gins. Sloe gin is traditionally made by steeping sloe berries (Prunus spinosa), also known as blackthorn, in gin in order to extract their flavor. It is often made in the home in small quantities but is also made commercially. In the commercial process, berries are harvested and frozen prior to shipment and use. The berries are then immersed in gin, the skins break on defrosting and liberate their juices into the gin, after which the product is sweetened with sugar, filtered and bottled. As an alternative to this traditional process, sloe gin may be made by a simple compounding operation using sloe flavors, gin and sugar. Orange and lemon gins are similar to sloe gin in that they are traditionally made by steeping the peel of citrus fruits in gin and the resulting extract is then sweetened with sugar. Pimm's, a gin-based drink in a category of its own, is compounded from gin, liqueurs and other secret ingredients and is usually decorated with fruit and drunk with lemonade.

Other Juniper-Based Drinks

Hollands gin, genever or Dutchtype gin is made by the redistillation of moutwijn (malt spirit) in the presence of juniper berries. This product, from which London dry gin developed,

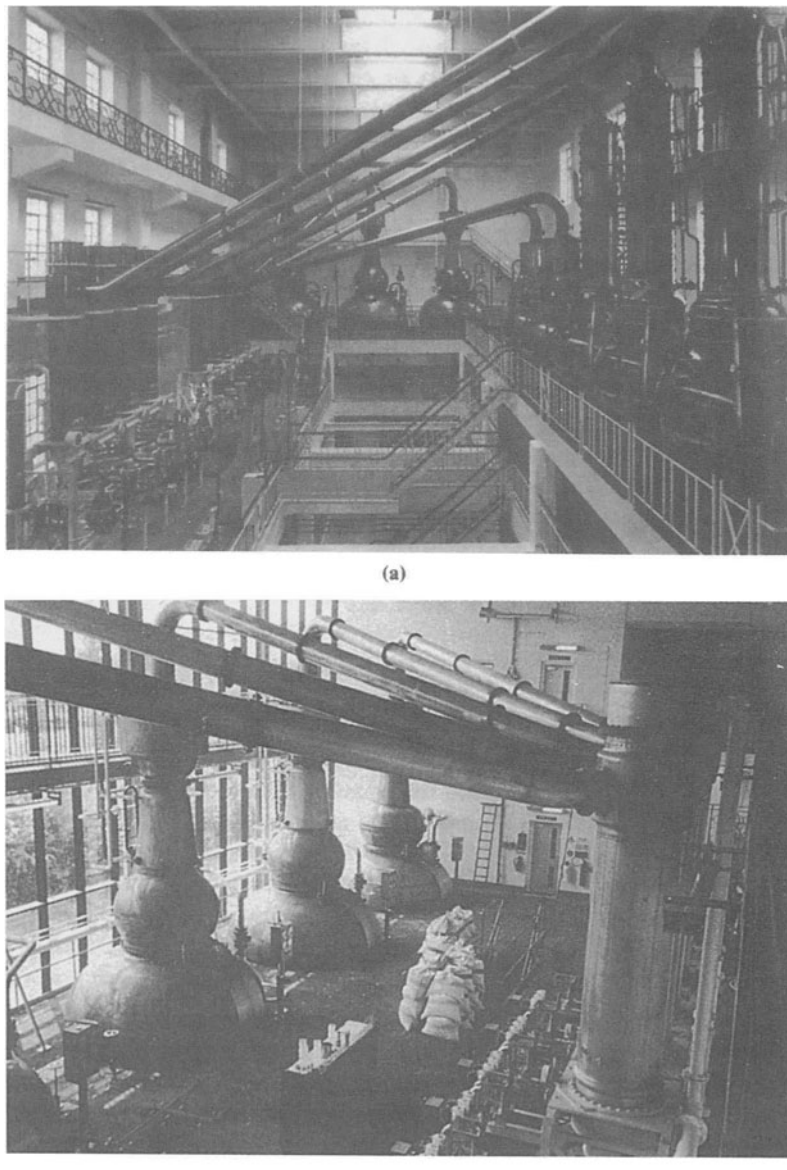


Figure 13–1 Two generations of gin distillery with a similar process. Top: London distillery of Tanqueray Gordon & Co. Ltd, opened in 1951 after its predecessor had been destroyed by bombs during the Second World War. Bottom: The latest distillery in Laindon, Essex opened in 1989.

is traditionally centered on the Dutch town of Schiedam. There are two forms of genever—jonge (young) and oude (old), a distinction related to the proportions of moutwijn used in the botanical distillation. A malted barley fermentation goes through up to three pot-still distillations to give the neutral moutwijn. Subsequent redistillation (which may include other

grain spirit) with juniper and other botanicals yields oude genever. Jonge genever contains less moutwijn together with neutral spirit to give a milder product which has the major proportion of the Dutch market in this category.

Steinhager is a form of wacholder, the German equivalent of gin. Steinhager is twice distilled from crushed fermented juniper berries. Other botanical materials may be included along with neutral alcohol. The juniper character of both genever and steinhager is low compared to London gin (Simpson, 1977).

Other Flavored Spirits

This section describes the flavored spirit production methods employed in the European Union. These are usually based on traditional methods. In less regulated countries and according to local definitions, products of a similar style may be produced using natural, nature-identical and synthetic flavors in simple compounding operations.

Caraway-flavored spirits come mainly from Denmark and Scandinavia. Those products described as akavit and aquavit are flavored using neutral alcohol distillates of caraway (Carvum carvi) and/or dill (Anethum graveolens). Other flavorings, may be used, but the flavor of the drinks must be attributable to distillates of caraway and/or dill. Use of essential oils is prohibited.

Aniseed-flavored drinks are made from neutral alcohol flavored with combinations of star anise (Illicium verum), anise (Pimpinella anisum) and/or fennel (Foeniculum vulgare) using one of the following techniques:

- maceration and/or distillation
- redistillation of the alcohol in the presence of the seeds or parts of the plants specified
- addition of natural distilled extracts of aniseed-flavored plants
- a combination of these three methods.

The aniseed taste must predominate although other natural material may be used. Pastis also contains natural extracts of liquorice root (Glycerrhiza glabra) which itself contains colorants known as chalcones. Pastis is finally flavored with sugar at a concentration of < 100 g/l. The amount of aniseed used must be controlled so that the anethole concentration is between 1.5 and 2 g/l.

Ouzo, by definition, is made only in Greece. Its flavor comes from a distillation or maceration of aniseed and possibly fennel plus mastic from a lentiscus on the island of Chios (Pistacia lentiscus Chia). The flavor distillate is produced by a batch process in traditional copper stills at an alcoholic strength between 55 and 80 % v/v and represents at least 20 % of the alcoholic strength of the ouzo. Ouzo is flavored with sugar at a concentration of $<$ SO g/l and is colorless.

Bitter-tasting spirits, referred to as amer or bitter, are produced by flavoring neutral alcohol with natural or nature-identical flavoring substances to give the required taste.

Packaging and Distribution

Vodka, gin and flavored spirits packaging may be undertaken in any suitable plant, providing certain criteria are met, such as the availability of stainless steel reducing vats and good quality reducing water. This enables product distilled at one location to be transported to another for bottling. London Gin distilled in the UK is often exported at high alcoholic strengths in stainless steel tanks (typically holding up to 20,000 litres) for reduction and bottling locally. Such operations have the advantage of reduced costs relative to cased goods and also potentially reduced tariffs (through the addition of locally added value). Similarly vodkas distilled in one country are bottled in another.

In common with other distilled spirits, most vodkas and gins are packaged in glass bottles, the standard size being 700/750 ml, although miniature (50 ml), 500 ml and 11 sizes are particularly common in duty-free markets. Bottle closures are made from aluminum or plastic and in certain markets special fitments incorporating one-way valves are used on bottles in order to reduce the risk of illegal refilling.

PVC (polyvinyl chloride) was tested as a potential material for spirit bottles in the late 1970s but was unsuccessful because of its poor compatibility with spirits, migration of plasticisers into the product and concern at that time over the carcinogenicity of vinyl chloride monomer. In the early 1980s, plastic bottles made from PET (polyethylene terephthalate) were introduced for use in the airline trade. PET is a relatively inert plastic, which has proved to have good compatibility with spirits. PET bottles, typically in 50 and 500 ml sizes, have the advantage of being considerably lighter than glass and virtually unbreakable, a considerable advantage when used within an aircraft.

Vodka and gin are essentially very stable products (Warwicker, 1963). This characteristic has been achieved by careful selection of the botanical ingredients so that gin congeners remain dissolved in solution at bottling strength and by use of demineralized reducing water in order to eliminate risk of precipitate formation or foreign taste effects. There is no risk of microbiological activity in spirits at normal bottling alcoholic strengths.

A number of ready-to-drink mixed spirits have come on the market in recent years in the form of spirits mixed with soft drinks. For example, gin/vodka and tonic and vodka and cola mix. These mixed drinks are typically sold at between 5 and 10 % v/v alcoholic strengths and packaged in l50 ml glass bottles and two-piece aluminium cans. Their compositions reflect the individual ingredients, although an additional complication of their packaging is the need for carbonation during bottling/canning and a potentially finite shelf-life at relatively low alcoholic strengths and acidic pH.

ANALYSIS

The sensory and chemical analyses of flavored spirits may be based upon the three principal components making up the product, namely alcohol, water and flavors. These analyses find application in raw material assessment, production quality control, generic and brand authenticity analysis and competitor product analysis. The analytical régimes described are applicable to each of these three components individually as well as the finished product matrix. The nutritional value of non-sweetened flavored spirits such as gins and vodkas comes mainly from their alcohol content and is typically 222 kcal or 919 kJ per 100 ml (Holland et al., 1991). Other components are present at trace concentrations.

Alcohol

Analysis of alcohol used for vodka, gin and flavored spirits production involves sensory assessment, alcoholic strength measurement and specific chemical tests. Sensory assessment is normally conducted by nose against an approved reference sample. It is common practice to place a sample of the alcohol (typically 25 ml) in a tulip-shaped glass and cover with a watch glass for a few minutes before nosing by a trained sensory panel. Some panelists prefer to dilute the sample with water down to approximately 20 % v/v alcoholic strength before nosing.

Alcoholic strength measurement, traditionally conducted by hydrometry or pycnometry, is now more commonly undertaken on small volumes of test sample (5 ml) using a precision density meter such as the Anton Parr™ 55 and 58 or the Kyoto™ DA310 and DA510 models. These instruments have become commonplace in distilleries, and packaging plants during the 1980s following their acceptance by excise authorities for strength measurement for revenue purposes. Hydrometers are still commonplace, especially where large sample volumes are available such as in distilleries and vat rooms.

Specific chemical analyses are normally based on gas chromatography. As discussed in section 11.3, alcohol for gin and vodka manufacture must be neutral and free from trace congeners, which may impart a sensory character. Therefore, it is appropriate to conduct an analysis at the part per million levels for methanol, acetaldehyde, ethyl acetate and higher alcohols using direct injection gas chromatography with flame ionization detection. This analysis is useful for compar-

ing different alcohols, checking rectification and ensuring compliance with specifications. Many stationary phases and chromatographic conditions are available, one of the most popular phases being Carbowax™ 20M on Carbopack™ B (Martin *et al.*, 1981). The only peaks normally detectable in a good quality neutral alcohol are ethanol and trace methanol (Figure 13–2). Trace congeners, such as low molecular-weight ethyl esters, which may be associated with undesirable sensory character, can be determined by extracting into a non-polar solvent followed by gas chromatography on a polar Megabore™ or capillary column.

Various chromatographic and non-chromatographic procedures are available for checking compliance against the European Union specification. These are described in 'Community methods applicable in the wine sector for the analysis of neutral alcohol' (Official Journal of the European Communities, 1992). Although the methods are applicable to neutral alcohol derived from wine-spirit, the methods are also relevant to neutral alcohol derived from other carbohydrate sources.

Two procedures are of particular note. The first is the determination of permanganate clearing time. This test is based on the time required for a standard solution of potassium permanganate in a test spirit sample to fade to a set color at 20 °C. The test assumes a relationship between the reducing capacity of the spirit and odor quality, the former being influenced by the presence of trace congeners, particularly those containing double bonds (Simpson, 1977). Sensory assessment and trace gas chromatographic methods now tend to replace this older method in routine quality analysis. The second method of note is the determination of ^{14}C in ethanol, a test which permits a distinction to be made between alcohol of agricultural origin (fermentation alcohol) and alcohol derived from fossil fuels (synthetic alcohol). Although this test is rarely required by most manufacturers, it can be useful in the overall portfolio of tests when considering a new source of neutral spirit. The natural ^{14}C content in the atmosphere, which is absorbed by living vegetation by assimilation, is a varying (but referenced) value. This value will be reflected in fermentation alcohol but ^{14}C will not be detectable in synthetic alcohol, as all natural radioactivity will have decayed to zero during its period as a fossil fuel source prior to extraction and synthesis as industrial alcohol.

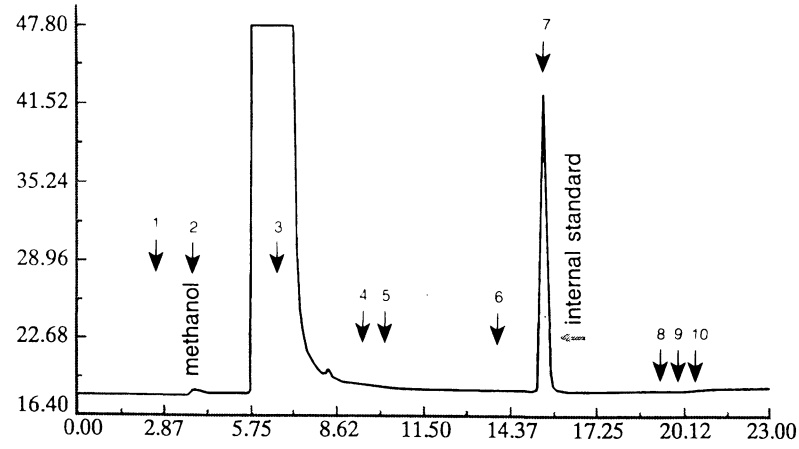


Figure 13–2 A higher alcohol gas chromatogram for a good-quality neutral alcohol indicating the absence of congeneric material. The retention times of the cogeners of interest are marked on the chromatogram: 1, acetaldehyde; 2, methanol; 3, ethanol; 4, ethylacetate; 5, *n*-propanol; 6, isobutanol; 7, 3-pentanol (internal standard); 8, acetic acid; 9, 2-methyl butanol; 10, 3-methyl butanol. Limits of detection are < 0.5 g/100l alcohol.

Water

Water, which makes up approximately 60 % of a bottled spirit sample, consists of water present in the high-strength distillate or compounding plus water used in the reduction of that spirit to packaging strength. Process water from demineralization plant is normally monitored online by conductivity measurement against a preset specification, with conductivity increasing as anion and cation concentrations increase. Bulk demineralized water is also normally examined prior to process use by sensory analysis in order to check that it is odorless, clear and free from particulate matter. The pH of demineralized water normally ranges from 5 to 8. The pH of gin and vodka is also typically in this range unless any acidic material is added at the compounding stage. Trace cations, such as sodium, potassium, calcium and magnesium are normally monitored in process water at the low ppm (μg/ml) level by atomic absorption spectrophotometry with flame atomization. Ion chromatography is becoming increasingly used for the detection of trace anions.

Flavor

There is great variety in the sensory characteristics within specific categories of flavored spirits. Gins exhibit a range of characters on top of their alcohol and juniper base. Each of the botanicals will make a sensorial contribution depending on its source, concentration and relationship with other botanicals. Of particular note are the citrus characteristics from orange and lemon peel, the spicy characteristic from coriander and the earthy characteristic from angelica. The sensory character of vodkas can also vary on top of the alcohol base. This is obviously much less intense than that of gins and other flavored spirits, but is nevertheless discernible and no doubt related to trace congeneric material remaining in the distilled spirit. Other spirits, particularly those flavored with aniseed, have very strong flavor characteristics.

A vocabulary of 21 descriptive terms has been developed for gin flavor using an untrained panel. The resulting data were subjected to principal components analysis. The need for vocabulary refining and chemical reference standards to precisely define the meaning of each descriptive term was identified (Piggott and Holm, 1983).

Although sensory analysis is the key arbiter in the quality assessment of flavored spirits, botanical congener analysis provides a valuable fingerprint in the analysis of gin and other flavored spirits. It is not so relevant to the analysis of vodka unless the detection of trace distillation impurities and added flavorings are required. Botanical congener analysis is normally based on the extraction of botanical congeners into a non-polar solvent followed by a capillary column gas chromatographic separation with flame ionization detection.

This approach, using chloro-fluorocarbons (such as Freon 11) as extracting solvent with analysis by gas chromatography-mass spectrometry, has been used to identify the principal flavor volatile components in London Dry Gin (Clutton and Evans, 1978). This important work identified a range of compounds using mass spectrometry and chromatographic retention data. These included terpenes (α-pinene, sabinene, myrcene, (+)-limonene, γ-terpinene), terpineols (linalool, terpinen-4-ol, α-tepineol), and sesquiterpenes (α-humulene, γ-muurolene and δ-cadinene), etc., some of which could be associated with juniper, others with coriander seed oil and some with both (Clutton and Evans, 1978; Rogers, 1993).

The contribution of individual botanical materials in a distilled gin is illustrated in Figure 13–3. This work showed that many monoterpenes are contributed by both juniper and coriander, while terpinen-4-ol comes mainly from juniper and linalool, camphor and geranyl acetate come mainly from coriander. Juniper and coriander were distilled individually in the laboratory from ethanolic solutions. (Figure 13–3).

The volatile constituents of an alcoholic extract of juniper berries have also been shown to contain ethyl esters of long-chain fatty acids (Taskinen and Nykanen, 1976) and a similar range of terpenes have been reported in a steam

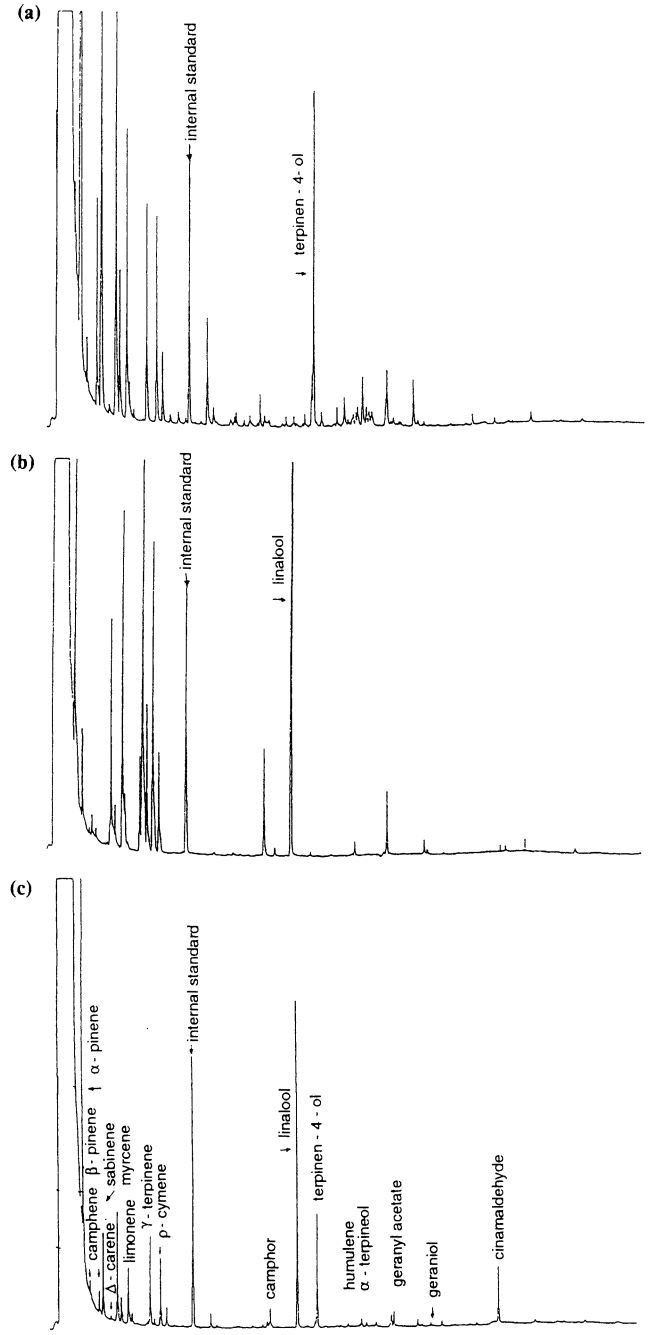


Figure 13–3 Capillary column gas chromatograms of ethanolic distillates of juniper (a) and coriander (b), together with a distilled gin (c). Analysis was by flame-ionization detection using a 25 m × 0.2 mm inside diameter CP57 CB fused silica capillary column (Chrompack) with on-column injection. The temperature program was 40 ° for 3 minutes and 40–180 °C at 6 °C/minute. All the distillates were extracted into carbon tetrachloride in the presence of ethyl heptanoate as internal standard.

distillation of juniper berries (Bonager and Galletti, 1985). Similarly, the major volatile flavor components of coriander seed oil have been investigated, with linalool being the major component detected (Heath, 1973). Interestingly, coriander leaf is rich in aldehydes (Macleod and Islam, 1976). Another paper has demonstrated that London dry gin is much richer in flavor compounds than products such as genievre or steinhager, where the higher fusel alcohols predominate over botanical congeners (Simpson, 1977).

Aniseed-flavored spirits are particularly rich in anethole, a compound detectable by either gas chromatography or reversed phase high-performance chromatography with UV detection. Compounds detected in gin, vodka and alcoholic beverages in general have been documented both by product (Maarse and Visscher, 1989; Ter Heide, 1986) and chemical type (Nykanen and Suomalainen, 1983). The essential oils of many of the botanical components associated with flavored spirits have also been analysed by gas chromatography and mass spectrometry (Masada, 1976).

Brand Authenticity Analysis

Authenticity issues affect many products including food and beverages. A popular brand of vodka or gin may be illegally substituted in the on-trade by another, usually cheaper brand. This results in the consumer being deceived and the producer of the genuine brand losing business. In order for enforcement agencies to apply appropriate consumer protection laws, analytical evidence is required to check the authenticity of suspect samples.

Brand authenticity analysis for vodka is problematic due to the general absence of components, which may act as authenticity markers for a particular brand. However, as mentioned earlier, a number of popular vodkas contain additives such as glycerol, propylene glycol and sug-

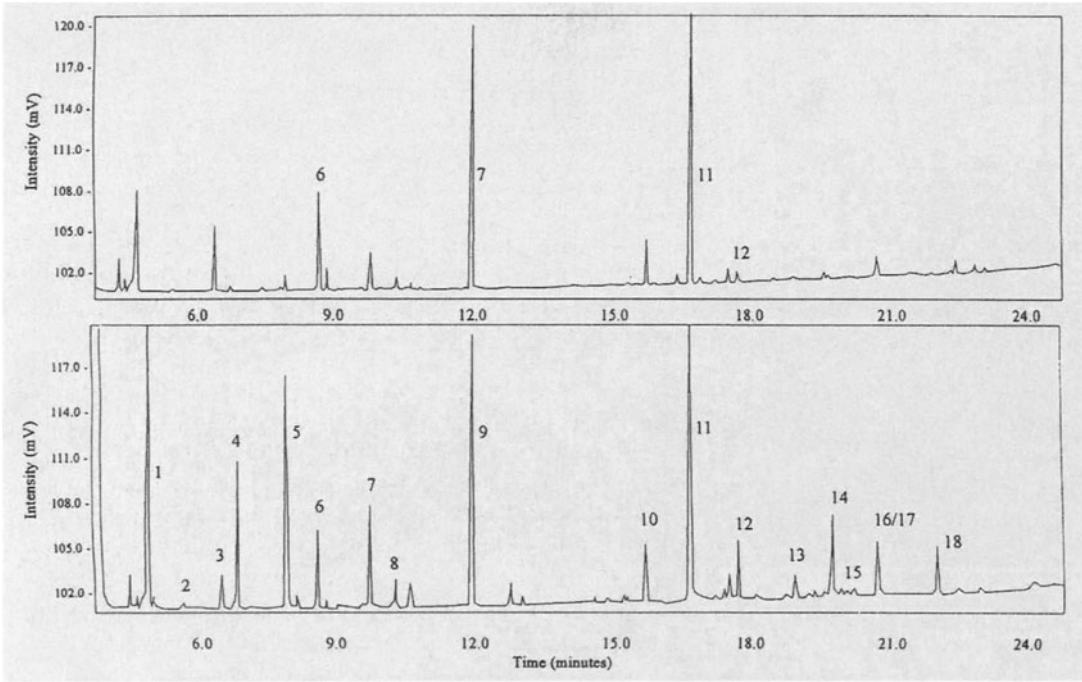


Figure 13–4 Example of a brand authenticity analysis showing capillary column gas chromatograms of extracts of a suspect gin sample (upper) compared to a reference sample of Gordon's Gin (lower).

ars and these may be used to facilitate brand authenticity analyses (Table 13–6).

The gin botanical congener profiles of selected gins have been shown to produce brand specific consistent chromatographic patterns and quantitative range data over many successive production batches. The equivalent results for suspect samples may then be compared with reference data in order to check for brand authenticity. Visual comparison of the chromatographic profiles of suspect and reference samples is also appropriate with most attention being paid to the non-volatile congeners (Figure 13–4). The non-volatile congeners (based principally on terpineols and sesquiterpenes) elute in the chromatographic separation after ethyl heptanoate internal standard and are stable in gin. The mono-terpenes are more volatile and to evaporate from product with time, thus making them less useful in authenticity analyses (Aylott, 1995).

Finally, generic authenticity analysis is required to check whether a specific product meets the requirements of the spirit category under which it is sold. In such cases, data from the analyses described above are related to the requirements of the generic definition. Typically, these would include the requirements of neutral alcohol for vodka and gin and botanical congeners derived from juniper for gin.

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14

Liqueurs & Speciality Products

David W. Clutton

INTRODUCTION

'Speciality Products' is an all-embracing term that can be used to cover a wide variety of alcoholic drinks, cocktails and aperitifs etc. Any spirit-based product, which is *not* itself a legally-defined spirit or liqueur, and which cannot be categorised otherwise, could easily be classified as a 'speciality'.

Liqueurs are undoubtedly the most common type of speciality product. The word liqueur is thought to derive from the Latin phrase *lique facere* meaning 'to melt' or 'to dissolve' (Hallgarten, 1983). Liqueurs are normally produced by dissolving or blending several components together. The number and style of such products is legion, varying from high strength 'traditional' liqueurs through to lower strength 'speciality' brands, cream liqueurs, aperitifs, and mixed drinks. Most of the traditional liqueurs contain 35–45 % alcohol by volume, but many of the newer brands are less strong. Cream liqueurs—an important sector—are often regarded as self-indulgent products and most liqueurs are still perceived by many consumers as 'luxury goods'. Aperitifs without alcohol and *no-alcohol* 'liqueurs' are also now being developed. Brands such as *Funny Light* from Belgium contain 0 % alcohol, as do UDV's North American no-alcohol 'Arrow' cocktail range extensions. But their success is somewhat erratic. Aromatic Bitters are popular in Central and Eastern Europe and some brands sell significant quantities (e.g. Campari: 2.90 m cases; Jägermeister: 2.47 m cases; Fernet Branca: 2.00 m cases in 1998).

The more traditional liqueurs are often consumed after dinner or at specific times of year (e.g. Christmas) and the principal sales period for many liqueurs is still during the months of November and December. However, consumers are now becoming much more adventurous in their drinking habits and the range and mixability of many liqueurs now leads to a broader spectrum of consumption patterns. However, in order to develop market share, many of the traditional liqueurs still need to be 'deseasonalized'. This remains the key objective of many marketers in the industry. Typical liqueur consumers are female, single, 25–45, and ABC1 socio-economic status.

Speciality products is essentially the category of ***brands***. It is also a term often applied to liqueurs or other products which are intended or

designed to be flexible in usage pattern, to help improve their image of versatility i.e. 'more than a liqueur'. The market positioning of Liqueurs and Speciality Products (LSPs) is extremely important if they are not to become staid and 'too serious'. Indeed some of the lower-strength 'ready to drink' (RTD) products, which may be based on branded liqueurs or spirits, are specifically marketed to contain a fun element. LSPs are extremely versatile, usually have pleasant taste characteristics and are easily consumed by most people, unlike some of the more traditional spirits (e.g. whisky) which might be considered, by some, to be an 'acquired taste'.

The LSP sector is, at times, extremely fickle in nature. Many products fail after a very short lifespan. Brands such as Monterez, Misty, Bezique, Greensleeves, and Topaz all existed somewhat transiently, but are no more. There are innumerable and many extremely imaginative ideas for liqueurs which never find their way to market, let alone succeed. All brands need a unique selling proposition (USP) to 'add value' for the consumer and to become successful. It is facile to mix together alcohol, sugar, flavoring and coloring and add a 'fantastic' brand name. Such a product is unlikely to be a winner without a unique point of difference that can be identified and recognized by the consumer. Heritage and a credible 'storyline' are paramount for success. But persuading customers to try new brands may at times be difficult. Most consumers simply do not know what they want from a product. This is why effective Marketing is the key to real success.

The life-cycle of some LSP brands may realistically be no more than 3–4 years. Others which have achieved greater success (e.g. Bailey's Original Irish Cream) flourish and become, in some sense, 'traditional' although this evolutionary process must be very carefully monitored and manipulated by the marketers. Generally speaking, the first product in a specific market sector usually holds on to the lion's share.The vogue for novel styles of liqueur (e.g. clear/colorless spirits without caramel coloring) can also be somewhat fickle since many consumers are not genuinely concerned about 'purity/no additives'; they might claim to believe the philosophy, but many seldom live it out in the real world.

Innovative design and packaging undoubtedly play an increasingly important role in the success of new LSP brands. Unique bottle designs are very prevalent in the LSP sector. Good, well-established examples are Malibu and Sheridan's. However, increasing environmental pressures are now leading to revised thinking during the packaging design process. Weight of bottles, recyclability and improved tamper-evidence in particular are all vital considerations for any new brand. Sponsorship in the advertising of LSPs is common and advertising budgets are often significant. The rules governing advertising vary widely from country to country. For example, use of TV advertising in the UK was, until very recently, not permitted. Cinema and cable/satellite TV advertising is developing significantly, particularly with the growth in digital channel television.

STATISTICS

Global consumption of LSPs is enormous. In 1998 some 70+ million equivalent cases (based on 12 × 0.75 litres i.e. 9 litres per case) were sold. The world's top selling brands are listed in Table 14–1.

Bailey's Original Irish Cream dominates the global liqueur sector with annual sales of 4.2 million cases. This is the worlds largest-selling single brand of liqueur. The world market for cream liqueurs has been estimated (Euromonitor) to be around 150 million litres which certainly keeps the cows extremely busy!

The preference for specific LSPs is market-dependent. Thankfully, not all countries have the same taste preferences and this presents an exciting challenge for the marketers and product development professionals. 'Duty-free' sales at ports and airports have traditionally been an important sector, but with the demise of duty-free in the European Union, this modified sector presents a new marketing challenge.

Table 14–1 World's Top Brands of LSPs (Drinks International Bulletin, 1999)

Brand	*Category*	*Company*	*1998 m 9 litre cases*
De Kuyper range	Liqueurs/schnapps	Koninklijke De Kuyper BV	4.29
Bailey's Original Irish Cream	Liqueur	Diageo	4.20
Kahlúa	Liqueur	Allied Domecq	2.90
Campari	Bitter/aperitif	Davide Campari	2.90
Jägermeister	Bitter/aperitif	Mast-Jägermeister AG	2.47
Berentzen range	Liqueurs	I B Berentzen	2.40
Southern Comfort	Liqueur spirit	Brown-Forman	2.17
Fernet Branca	Bitter/aperitif	Fratelli Branca Distillerie	2.00
Malibu	Liqueur	Diageo	1.80
Di Saronno Amaretto	Liqueur	ILLVA Saronno SpA	1.61
Fernet Stock	Bitters	Eckes AG	1.60
Bols range	Liqueurs	Koninklijke Bols NV	1.53
Marie Brizard range	Liqueurs	Marie Brizard et Roger Intl	1.40
Grand Marnier	Liqueur	Marnier-Lapostolle	1.30
Suze	Bitter/aperitif	Pernod Ricard	1.15
Hiram Walker range	Liqueurs	Allied Domecq	1.15
Cointreau	Liqueur	Rémy Cointreau	1.06

USA: The top twenty single brands in the USA (1998) are given in Table 14–2. Many companies also produce a range of branded LSPs. In the USA the 'De Kuyper' brand, which sold 2.446 million cases in the USA in 1998, has 44 flavour variants, with Peachtree Schnapps being the biggest seller. Other branded ranges of cordials include Hiram Walker (1.040 m.cases), Jacquin, Arrow, Bols (29 variants), Gaetano, Phillips, Boston, Allens and Paramount. The total cordials and liqueurs market in the USA was estimated to be 16.17 m. cases in 1998. During the boom of the late 1980's approximately 25 new LSPs were introduced each year which illustrates the immense competition and perceived opportunity in the sector. In the USA, liqueurs represent about 11 % of total spirits volume, being behind only Vodka (1st) and Canadian Whisky (2nd).

Europe: The European liqueur market is said to support around 500 different products, but is effectively dominated by a handful of top brands, including Tia Maria (30 % +) and Cointreau (20 %). Both of these successful brands have been strongly advertised and promoted to encourage the consumption of traditional liqueurs on a more flexible year-round basis e.g. 'on ice'.

Spain: Nationally produced brands dominate the scene. '*Ponches*'—sweet, wine-based products—sell around 1 million cases per annum and Pacharán sells around 1.3 million. Every region of Spain has its own style of liqueur and many are produced specifically for religious festivals. *Chupitos*, sweet liqueurs served free in many restaurants, are usually apple or peach flavored schnapps-type products and most are domestically produced.

Italy: Brands such as Genepi, Strega, Mandarinetto perform well. Grappa (a spirit distilled from fermented pressed grape skins) sells around 20 million litres per annum. Amari bitters (e.g. Averna) and numerous other brands are also popular. Herbal punches and flavoured vodkas are also fashionable. Sambuca is the liqueur sector leader. Cointreau, Di Saronno Amaretto, Zabov and Bailey's are also very popular.

France: Domestic and international brands both perform well. 90 % of all pastis sales are in the French domestic market, dominated by Pernod Ricard. GET 27 (peppermint) is also popular, holding around 9 % of the French

Table 14–2 Top Twenty brands of LSPs in the USA (millions of 9 litre cases) (Adams Liquor Handbook, 1999)

Kahlúa	1.335
Southern Comfort	1.185
Bailey's Original Irish Cream	0.890
Alize	0.600
Jägermeister	0.500
Grand Marnier	0.380
Di Saronno Amaretto	0.265
Rumpleminze	0.252
Yukon Jack	0.250
E&J Cask & Cream	0.235
Goldschläger	0.235
Carolans	0.232
Romana Sambuca	0.223
Kamora	0.216
Frangelico	0.192
Emmet's	0.190
Tequila Rose	0.186
DuBouchett	0.165
Mohawk	0.160
Dr. McGillicudy's	0.140

liqueur market.There is no 'national' taste in liqueurs, taste preferences being somewhat regional. Peach schnapps is gaining in popularity. Cassis remains popular and is used to produce the classic 'Kir' aperitif (Cassis and Champagne).The total liqueur market represents around 11 % of total alcohol consumption in France. Anis (pastis) is the largest category at around 40 % of total with whisky, gin and vodka accounting for 22 %.

Germany: Here a strong market exists for 'Korn' spirits that are produced from cereals, at 32 % vol. alcohol or sometimes higher. Many products such as fruit schnapps are based on a korn or vodka base, mixed with fruit extracts. The strength of such products normally lies between 17 and 29 % vol alcohol. Apfelkorn (apple) is the market leader. Other flavors include cherry, strawberry, blackcurrant and plum. Additional important sectors include Halbitter liqueurs, fruit and bitter liqueurs, Advocaat, Cream liqueurs and Coconut liqueurs.

United Kingdom: LSPs are the fastest growing sector of the trade. The LSP market represents approximately 10 % of the total UK liquor market. From a total of 2,039 thousand hectolitres (40 % vol) produced, LSPs account for 198,000 hl; cocktails and aperitifs 16,000 hl. (Source: UK HM Customs & Excise). Innovative product development and strong marketing activity have been the key to success in this sector. Cream liqueurs are extremely popular, as are speciality drinks such as Mirage and Taboo.

Pre-mixed drinks

Pre-mixed spirit-based drinks (also referred to as RTDs . . . Ready To Drink; Alcocarbonates; FABs . . . Flavored Alcoholic Beverages; or PPSs . . . Premium Packaged Spirits) are growing in popularity in most European countries. Such products usually contain around 5 % vol alcohol. Sales in the UK during 1998 were estimated to be 4.8 million cases. Despite some marketing disasters, and sometimes extremely fickle branding, the sector has shown growth and some premium brands are performing extremely well. 'Bacardi Breezer', the best selling PPS brand, sells around 3 million cases p.a. The brand has several flavor variants including watermelon, peach and lime. Pre-mixed Gin & Tonic (10 % alc.), Bacardi & Cola, Jim Beam (Bourbon) & Cola (5 % alc.), and Martini's 'Anytime' (Vermouth & Tonic) are some of the other brands which have shown growth. Other significant brands include Hooch, Smirnoff Mule and Malibu Spice. 'Two Dogs', the brand which fired the growth in the RTD category in the UK, has since all but disappeared.

The attraction of RTDs lies in their convenience and refreshment values. Specifically, they provide fun and excitement for younger drinkers and allow them to experiment with differing taste sensations. Despite some early adverse publicity regarding the potential for 'under-age' drinking, which was allegedly fuelled by the growth in the RTD sector, the majority of young consumers do actually drink responsibly. The PPS brands also serve as a gentle introduction for many consumers to the core spirit brands and provide a bridge between adolescent and adult

drinking patterns. Many of the core spirits such as Scotch Whisky, Brandy and Dark Rum may be perceived by some new consumers to be fairly 'difficult' to drink due to their basic sensory characteristics. And indeed, Scotch whisky is perhaps an 'acquired' taste requiring some practice. However, if the core spirit is used as a base for an RTD brand, the taste properties can be somewhat ameliorated. Due to the current intense marketing competition from the beer market, RTDs (in particular PPSs) offer one way of revitalizing long term growth in the core spirits sector, particularly amongst emerging consumers. In the USA, pre-packaged prepared cocktails sell approximately 5.9 million cases per year. Leading brands include TGI Fridays, Chi-Chi's, Club, IceBox, Drinks to Go, and other 'wine-cooler' type brands.

LEGAL DEFINITIONS

Liqueurs are, by definition, sweet flavored spirits that may be either colored or colorless. In the United States they are normally referred to as 'cordials'. In France they are called 'digestifs'. Many of the older and more classical liqueurs are of monastic origin and have been produced for several hundred years. The origins of many are lost in the mists of time. Until recently, liqueurs were produced according to traditional methods and practices without much legal control. Nowadays their classification is more well defined, particularly in Europe and the United States.

Under European Council Regulations (EEC 1576/1989) a liqueur is defined as: '*A spirit drink having a minimum sugar content of 100 g/litre (as invert) produced by flavouring ethyl alcohol of agricultural origin, or a distillate of agricultural origin or one or more spirit drinks, sweetened, and possibly with the addition of products of agricultural origin such as cream, milk, or other milk products, fruit, wine or flavoured wine*'. The additional descriptor '*Crème de*' followed by the name of a specific fruit, or raw material used, excluding milk products, is reserved for liqueurs with a minimum sugar content of 250 g/litre (as invert). '*Crème de Cassis*' may only be used to describe blackcurrant liqueurs that contain at least 400 g/litre sugar. Since liqueurs are a sub classification of 'spirit drinks', they must also contain at least 15 % alcohol by volume (at 20 °C). In practice liqueurs are produced with strengths ranging from 15–60 % alcohol, although most contain 20–50 % vol.

In the USA the manufacture and definition of liqueurs is controlled by the Bureau of Alcohol, Tobacco and Firearms (BATF). Under Federal Regulations (BATF, 1999), liqueurs and cordials are defined as: '*Products obtained by mixing or re-distilling distilled spirits with or over fruits, flowers, plants or pure juices therefrom, or other natural flavouring materials, or with extracts derived from infusions, percolation or maceration of such materials and containing sugar, dextrose or levulose, or a combination thereof in an amount not less than 2½ % by weight of the finished product*'.

The definitions in Europe and the USA are therefore significantly different, particularly in terms of minimum sugar content. The definitions are, however, both fairly broad, which allows a wide variety of liqueurs to be produced.

There are currently no formal compositional regulations governing lower strength/mixed/cocktail type drinks within the EEC. In the UK such products must always meet the requirements of the 'Food Safety Act' (HMSO, 1990) and, of course, labeling must be legally acceptable (HMSO, 2002). Legislation is continually being developed to ensure that product descriptors do not mislead the consumer. Specifically, where generic spirits such as whisky, brandy, rum etc. are used for the alcohol base, there is an important distinction to be made between the original generics and diluted imitation products.

Specific restrictions also govern the use of flavorings in liqueurs and spirit products (EEC, 1576/1989). In the EU, flavorings are controlled and defined by regulation (EEC, 388/1988). If specific fruits or plant materials are referred to as part of the liqueur descriptor (including picto-

rial representation), these materials will, in general, need to be 100 % natural and at least 90 % derived from the specific plant material in question. If no specific mention is made to the 'natural' source of flavor, artificial (synthetic) flavorings may be used. In the USA '*boosted*' natural' flavors are allowed (BATF 1988/1999). This means that flavors may contain up to 0.1 % artificial (synthetic) flavor components and still be classified as '*natural*'. This arrangement allows slightly more flexibility than the European system. Regulations in other countries may also differ. It is therefore vital to check for appropriate legal compliance for any formulation when LSPs are being developed.

COMPOSITION

All LSPs are manufactured essentially from a key list of basic ingredients: *alcohol, sugar, flavoring, coloring, and water.*

The combination of these ingredients determines the style and balance of the product. Some LSPs may contain other ingredients such as cream, fruit juices, emulsifiers, plant materials etc. Lower strength speciality products (RTDs) may also contain carbon dioxide, preservatives, antioxidants etc. All additives are, of course, subject to legislation (EEC 1995, 95/2).

The ***alcohol*** *base* (ethanol) may originate from any fermentable *agricultural* material. In Europe this is a legal requirement under the Treaty of Rome (EEC 1957). Synthetic alcohol from petroleum is not allowed for use in alcoholic beverages. Its presence can be easily detected using modern isotope measuring techniques. (Krueger H.W., 1982). The alcohol base may itself contribute flavor to the final liqueur. Pot-distilled spirits such as brandy, rum or whisk(e)y contain a wide range of natural flavoring compounds (congeners) produced during the fermentation/distillation process and these, combined with other added ingredients, can result in an extremely complex aroma and taste sensation in the final product. Alternatively the alcohol can be neutral, distilled to high strength (96 % vol.) through multi-column stills; in this case the final style of the liqueur is governed solely by the addition of flavorings etc. during the manufacturing process.

The ***sugar*** *base* for liqueurs can be derived from numerous sources, the specific choice depending upon availability, legality, price, purity/color, and the final 'mouthfeel' characteristics required. For example, sucrose results in a much greater viscosity effect than glucose. Sugars used can include crystalline sucrose (from cane or beet); liquid glucose syrup (dextrose); HFCS (High Fructose Corn Syrup from maize); honey; or RCM (rectified concentrated grape must). As most sugars are somewhat insoluble in high strength alcohol, the basic production method for liqueurs generally requires that the alcohol base containing the flavor is at a relatively low strength prior to mixing with sugar, otherwise unstable deposits may occur. Artificial sweeteners (94/35/EC) are not currently approved for use in spirits and liqueurs.

The added ***flavoring*** element in liqueurs can originate from the direct use of natural plant materials such as herbs (barks, roots, seeds, and flowers) or from fruits (whole or peels). Alternatively, it can be derived from the addition of steam-distilled essential oils or natural/artificial flavoring extracts.

Natural extracts can be obtained by:

Infusion: steeping in warm alcohol (40 °–60 °C) for several days. This process is also known as 'digestion'.

Percolation: passage of cold or hot alcohol through a bed of botanicals on a batch or continuous basis.

Distillation: botanicals are allowed to macerate and then extracted using a pot still distillation in neutral spirit

or by any combination of these sources. Some extracts are matured in oak casks prior to use in final products.

Artificial (synthetic) flavors are used in some of the cheaper brands of liqueurs, but there is a growing trend towards natural, since this has positive consumer/marketing benefits. What consumers often fail to recognize, however, is

that artificial flavors are often more extensively tested for toxicological risk than many 'natural' flavours. Natural may not always mean 'safe'.

The ***color*** of liqueurs may derive directly from the use of plant materials such as infusions of fruits, seeds and leaves etc. However, some liqueurs are also colored using approved 'food grade' colors and restrictions on usage patterns are often governed by specific legislation. For example, the EU has an approved list of food colors (94/36/EC) and maximum levels/approved applications for these materials are documented therein. The term 'food grade' has no legal definition in the EU although it is a commonly used descriptor. In effect all food colors must conform to the appropriate EU Purity Directive (95/45/EC), and under UK law the onus is always on the producer to ensure compliance with the Food Safety Act 1990. Plain Caramel (E150a) is the most commonly used and most stable color for spirits and liqueurs. This can be used at *quantum satis* levels in spirit-based products. For the less common colors (red, blue, green etc.) specific synthetic colors can be chosen e.g. Carmoisine (E 122), Patent Blue V (E 131), Chlorophyll (E 140).

The ***water*** used for the preliminary stages of manufacture (distillation, maceration, extraction etc.) can simply be natural /domestic or spring water, without special treatment, provided that it complies with relevant European legislation (80/778/EEC; 98/83/EC). For reduction of products to bottling strength, a higher purity level is required, to avoid shelf life/stability problems often caused by inorganic ions (Clutton, 1992).

A typical water specification for liqueur/speciality spirit products is shown in Table 14–3. Water used for the reduction of product to bottling strength (approx. 20–40 % vol.) should normally be of such purity that the *final product* does not contain more than:

2.0 mg/l calcium
1.0 mg/l copper
0.3 mg/l iron (0.2 for brown spirits)
3.0 mg/l magnesium
3.0 mg/l zinc
10.0 mg/l sodium*
1.0 mg/l aluminium

These 'safe' levels are based on established levels for the generic spirits and will depend upon product pH, alcoholic strength, sugar level etc. In practice, all products should be tested for shelf life/stability on an individual basis.

There is very little data published in the scientific literature regarding the analytical composition of liqueur brands. Undoubtedly many international flavor companies have undertaken a great deal of investigative analysis into the composition of branded liqueurs and spirits, in order to assist in the creation of possible flavor substitutes. The complexity of formulation of many of the liqueurs, however, makes the analysis and subsequent interpretation of compositional information an extremely difficult task. Many brands still retain their 'secret' formulae. Whilst the composition of the main generic spirits (whisky, brandy, rum etc.) is now well documented (Maarse, 1989; Nyknen, 1983; Piggott—this book), as is the composition of many of the essential oils/plant materials (Fenaroli, 1975), the liqueurs *per se* have not been the favored subject of many scientific authors. Indeed, much of this information is obviously commercially sensitive.

Appendix Table 4 provides a summary of the basic composition of a wide range of LSP's together with their country of origin. Alcohol content, where quoted, is expressed as % volume at 20 °C. Some brands may not now be available commercially and are recorded solely for reference purposes.

CREAM LIQUEURS

Cream liqueurs have become phenomenally successful since their development in the mid-1970's. Bailey's Original Irish Cream Liqueur led the field and continues to occupy its premium position. The 1999 global market for cream liqueurs was estimated to be around 150 million litres with 36 % being sold in Eastern Europe, 24

*This sodium level can only be obtained using demineralization rather than softening.

Table 14–3 Typical water specification for LSPs

Taste	Neutral; absence of earthy/metallic/salty taste
Odor	No apparent odor; absence of chlorine/earthy/fishy notes
Clarity	Maximum 1 ppm silica (Sigrist)
Color	No obvious color; maximum absorbance 0.04 (100 mm cell; 420 nm.)
Bacteria/algae	0.01 M ethanol in the test water should show no growth after incubation at 25 °C for 7 days; samples for bacteriological testing must be sampled aseptically and examined within 24 hours
Conductivity	Less than 10μS; preferably less than 5 μS.
Free chlorine	Absent
pH	5.0–7.5 maximum, (values outside this range indicate ion-exchange resins are nearing exhaustion)

% in Western Europe and a further 32 % divided equally between North & South America.

The technology of cream liqueur manufacture has been widely studied over the past decade, notably by Banks & Muir from the Hannah Research Institute (Muir, 1988). Cream liqueurs contain milk fat, sodium caseinate, sugars, alcohol, flavorings and, in most cases, colour and an emulsifying agent. Most products contain approximately 40 % solids made up from 15 % butterfat, 3 % caseinate, 20 % sugar and 2 % non-fat milk solids. The stability of cream liqueurs hinges on an effective homogenization regime which reduces the fat globules to a size which ensures a stable emulsion and where 'creaming' does not occur. The milk fat globules in cream are typically 1–12 μm in diameter. When the formation of cream 'neck plugs' in unstable product occurs, this is generally due to inadequate homogenization regimes (Dickinson, 1989). A four-fold reduction in creaming rate is observed if the globule diameter is halved. Globule size needs to be reduced to around 2μm in order to ensure an acceptable shelf life. If the majority of fat globules are reduced to a diameter of < 0.84 μm, creaming in liqueurs can be prevented for periods up to 3 years at ambient temperature.

The shelf life of cream liqueurs, particularly at higher temperatures, can be further improved by removing the potential for calcium-induced aggregation, by complexing residual calcium ion activity in the cream phase. This is normally achieved by the use of trisodium citrate at around 10 mmol/L. Although citrate is very effective at pH 6.8–7.0, its efficacy is reduced at lower pH. Many cream liqueurs show significant flocculation when mixed with acidic carbonated drinks (e.g. lemonade) due to inadequate buffer capacity and rapid release of carbon dioxide.

The basic manufacturing process involves the addition of cream, sugar and alcohol to a solution of sodium caseinate followed by homogenization at about 55 °C and 300 bar. The homogenization stage is normally performed twice in order to ensure emulsion stability. The mixture is then cooled; color and flavoring are added and the product is bottled. Most cream liqueurs contain 17 % alcohol and therefore bacterial spoilage is not usually a problem. The typical shelf life for most products is around 18–24 months at ambient temperature. It is not necessary to store most cream liqueurs in a refrigerator since they have adequate consumer shelf life at ambient temperature. The tremendous success of cream liqueurs has notably affected the sales of Advocaat, case sales of which fell by 56 % between 1984 and 1992. A number of cream liqueur brands are listed within Table 4.

COCKTAILS

Every era has its own individual cocktail combinations. The 20's brought the 'Stinger' and the 'Silver Bullet'; the 60's brought the 'Gimlet' and the 'Vodkatini'; the 70's disco era brought the 'Zombie' and the 'Harvey Wallbanger'; and the

80's saw the birth of the 'Tequila Slammer' and 'Margarita'. In the 90's, consumption of higher strength liqueurs as 'shooters' became fashionable. These drinks, which originated in Canada and the USA, are either single high strength liqueurs or may also be layered combinations served in small glasses and drunk in one quick gulp. Some of the most popular shooters are:

Fuzzy Navel	Peach schnapps, Vodka and Orange juice.
DOA	Parfait Amour, Anisette, Tequila.
Earthquake	Gin, Rye whiskey, Pernod.
B-52	Kahlúa, Grand Marnier, Bailey's Irish Cream.
Killer Bee	Vodka, Jägermeister, Barenjager.
Mind Eraser	Vodka, Kahlúa, Soda.
Sex on the Beach	Vodka, Peach schnapps, Cranberry & Orange juices.
Zipperhead	Vodka, Chambord, Soda.
Jawbreaker	Cinnamon schnapps, Tabasco.
Russian Rush	Vodka, Frangelico, Bailey's Irish Cream.
BBC	Bailey's Irish Cream, Bénédictine, Cointreau.

Pousse-Cafés are also popular. These are drinks that achieve rainbow layers of color by pouring assorted liqueurs and spirits into tall glasses. One example is the 'Flaming Lamborghini' which contains Grenadine syrup, Galliano, Sambuca, and Green Chartreuse. The cocktail is set on fire in the glass and the consumer attempts to drink it as quickly as possible through a straw; occasionally the bartender might add Blue Curaçao, Kahlúa and nutmeg for extra 'kick'!

SUMMARY

LSPs represent an extremely varied sector of the global drinks portfolio. With the move towards lower alcohol content products and increased refreshment values, the challenge presented to product development and technical personnel is both exciting and rewarding. There will always remain the niche opportunity for luxuriant brands; but technical issues such as shelf life, legality and environmental constraints etc. also need serious consideration during the development/crafting process.

Table 4 (Appendix)

THE COMPOSITION OF SOME LIQUEURS & SPECIALITY PRODUCTS

Product/ Brand	*Origin*	*Description*
Abricotine	France	Apricots and sweet almonds in brandy base. Yellow. Created in 1859 at Noyon.
Absinthe	France	Absinthe contained the toxic plant *Artemisia absinthum* (wormwood); this is currently illegal in the EU but is again now available from other countries; strengths vary from 60–85 % vol. Anise liqueurs have largely replaced absinthe.
Adam Tas (Van der Hum)	South Africa	Tangerine.
Advocaat	Netherlands	Egg yolks; min. 150 g/L sugar; brandy and vanilla. Min 14 % alc. Must contain minimum 140 g/L egg yolk. Popular brands include Warninks, Cooymans, De Kuyper, Keelings and Bols. Originally made from the abacate fruit in Brazil.
Afrikoko	Sierra Leone	Chocolate and Coconut.
Aftershock	USA	Hot and Cool Cinnamon liqueur. Red in color. Citrus version is blue. 40 % alc. Contains sugar crystals which grow with time. Jim Beam.
AGWV	Netherlands	Distilled from Bolivian cocoa leaves; contains Brazilian guarana, ginseng and herbs; 30 % alc.
Aiguebelle	France	Contains 50 herbs; green/yellow variants. Liqueur of 'Frère Jean'.
Alchermes Alkermes	Italy	Orange Flower extract, nutmeg, cinnamon, clove, coriander in brandy base. Originally contained fruits from the kermes oak (later found to be insects).
Alizé	France	Passion fruit/Cognac.
Allash	Russia	Sweet kümmel with bitter almonds & aniseed. Named after a castle in Latvia.
Alpen Cream	Switzerland	Coffee, brandy & whisky base.
Amadeus	Austria	Almond & Orange distillates with mature Cognac; 26 % alc.
Amanda	Netherlands	Neutral spirit/caramel base; 2 % fat.
Amaretto	Italy	Bitter Almond (*Prunus amygdalus amara*) and apricot kernels. Di Sarronno, Barbero, Giffard, Luxardo and Stock are well known brands.
Amaro	Italy	Liqueur bitters. Dark brown in color, containing herbs, bark extracts and botanicals. Averna (35 % alc.) is the best selling brand in Italy.
Amarula Cream	South Africa	Launched 1989; fruit of the African Marula tree (similar to mango). Fruit is pulped, sweetened, fermented and distilled in copper pot stills to 65 % alc and matured in oak casks for 3 years; 17 % alc.
Amour en Cage	Canada	Cherry.

Product/ Brand	*Origin*	*Description*
Amourette	France	Violet in color.
Anesone	Italy/ USA	Anise/ Liquorice.
Angelica	Spain (Basque)	Angelica & Pyrenean plants.
Angelikalikoer	Germany	Angelica.
Angostura	Trinidad	Aromatic bitters invented in 1824 by Dr. Johan Gottlieb Benjamin Siegert while serving as an army surgeon in Angostura, Venezuela. Traditionally used in 'pink gin'. 45 % alc. Does not contain angostura bark. Based on gentian and vegetable extract.
Anis	Various	Flavor derived from anise (*Pimpinella anisum*) and/or Star anise (*Illicium verum*) and/or Fennel (*Foeniculum vulgare*). Anise brands can be dry (*secco*) or sweet (*dulce*)
Anise del Mono	Spain	Aniseed.
Anisette	France	Aniseed/aromatic herbs including coriander; liquorice taste. White or red in color. Marie Brizard brand contains green anise, dill, fennel, iris and citrus fruits.
Aperol	Italy	Bitter orange and herbs. 11 % alc. apertif.
Apry	France	Apricots and brandy.
Archer's Peach County	UK/ Canada	Peach schnapps.
Ardine	France	Apricots macerated in alcohol. From the Bardinet company.
Arquebuse	France	Herb digestif liqueur.
Arrack (*Arack; Arraki; Aruk; Arrak; Raki*)	Arabic origin	The word means 'juice' or 'sweat/ perspire'. Made originally from date palm juice. Nowadays produced from distilling grapes, sugar cane, rice or dates; or from palm wine. Can be dry or sweet.
Ashanti Gold	Denmark	Chocolate.
Atholl Brose	Scotland	Invented 1475. Malt whisky, oatmeal, honey and cream; now herbs and 12-year-old whisky.
Aurum	Italy	Herbs & oranges in brandy base. Pale gold color.
Avalanche Blue	USA	Peppermint schnapps; 40 %; Jim Beam.
Averna	Italy	Amaro Siciliano herbal liqueur.
Baerenfang	Germany	Honey, Lime & Mullein flowers.
Bahia	Brazil	Coffee/grain spirit.
Bailey's Original Irish Cream	Ireland	Chocolate and Irish Whiskey. The first cream liqueur and now the world's No. 1 liqueur.
Bailey's Light	Ireland	Low fat version of the popular Bailey's Original Irish Cream Liqueur.
Banadry	France	Banana.
Barack Palinka	Hungary	Apricot.
Barenjager	Germany	Known as 'bear trap liqueur' in Medieval times; honey flavored.
Baska	France	Coffee.
B+B DOM	France	Benedictine DOM plus Cognac (1:1).
Becher	Czech Rep	Bitter based liqueur from Karlovy Vary region.
Becherovka	Czech Rep	Bitter based liqueur from Karlovy Vary region. (Pirnod Ricard)

Product/ Brand	*Origin*	*Description*
Beerenburg	Netherlands	Bitters made from 15 herbs, including angelica, gentian, violet and bay. 30 % alc.
Bénédictine DOM	France	Herbs in a brandy base. Formula includes 27 plants such as aloes, ambrette, apricot kernels, arnica, maidenhead fern, melissa, cardomom, cinnamon, cloves, juniper, lemon, nutmeg, pine kernels, tea, thyme, vanilla, myrrh, saffron, angelica, coriander, yarrow, hyssop with honey. Originated by Benedictine monk Dom Bernardo Vincelli of Fécamp (1510); abbey destroyed by fire in 1789; revised product revived in 1863 by Alexandre Le Grand. DOM is abbreviation of *deo optimo maximo* (to God most good, most great); 40 % alc; 320 g/L sugar. Colored with caramel and saffron.
Berentzen Apfel Korn	Germany	Apple fruit and wheat spirit schnapps. 20 % alc. Other variants include Grüner Apfel, Saürer Apfel and Winter Apfel spiced with cinnamon.
Berenburg	Germany	Gentian root, Juniper berries and Laurel leaves; max. 20 g/L invert sugar; minimum 30 % alc.
Bescen	Netherlands	Blackcurrant gin liqueur from De Kuyper.
Black Mountain	Wales	Fruit and herbs; 30 % alc.
Black Russian	Netherlands	Coffee and grain vodka pre-mix from De Kuyper. 14.5 % alc.
Black Sun	Germany	Siberian ginseng root and wild blackberries in a vodka base. 16.6 % vol. Puschkin brand.
Bocksbeeren	Eastern Baltic	Blackcurrant.
Boggs	USA	Cranberry; red in color.
Bols	Netherlands	Famous company founded in 1575 by Lucas Bols. Range of liqueurs including Bols Blue (a Curaçao made from a recipe that includes Kinnow fruit—a mandarin orange from Pakistan). Bols range has 29 flavors including Cherry Brandy, Red Orange, Coconut, Raspberry, Strawberry, Kiwi, Vanilla, lychee etc. Typically 24 % alc.
Boswandeling	Netherlands	Coconut, banana, guarana and sour cream. 15 % alc.
Boukha	Tunisia	Fig.
Brancamenta	Italy	Mint version of Fernet Branca.
Braulio	Italy	Alpine Herbs; bittersweet taste.
Brûlé	UK	Chocolate Cream.
Brontë	UK	Yorkshire liqueur; brandy, honey, herbs & spices.
Buttershots	USA	Caramel flavor schnapps from De Kuyper.
Cacao mit Nüss	Germany	Hazelnuts & chocolate; colorless.
Cactus Juice	Netherlands	Schnapps for making Tequila-based 'Margaritas'.
Café Marakesh	Netherlands	Coffee liqueur; 23 % alc.
Cafka	Mexico	Coffee liqueur from Cordoba, Mexico
Calisaya	Spain	Bitters with cinchona bark and other herbs in a brandy base; pale golden brown color.
Campari (Bitters)	Italy	Blend of 68 different aromatic and bitter herbs infused with bitter orange peels, Chinese rhubarb, cinchona bark and quinine in neutral spirits; red in color.

Product/ Brand	*Origin*	*Description*
Canton Delicate Ginger	China	Six varieties of Ginger with other herbs, honey and ginseng; spirit and brandy base; 20 % alc; produced in Guangdong province.
Can-y-Delyn	Wales	Whisky-based, herbal
Capucine	Austria	Coffee/Cream.
Capricornia	Australia	Tropical fruits from the Tropic of Capricorn.
Caramela	France	Fran Vedrenne in Burgundy.
Cardamaro	Italy	Bitter herbal tonic liqueur
Carlsbad	Czech Republic	Bitter liqueur speciality, first produced as a stomach medicine in 1805.
Carlsberg	Czech Republic	Slightly bitter.
Carmeline	France	Neutral spirit/herbs. Green/Yellow; no longer produced.
Carmelitano	Spain	Herbs in brandy base.
Cartron No. 7	France	Raspberry, cherry, blackcurrant and other red fruits from Burgundy.
Cassis	France	Blackcurrant; Appellation Contrôlée from 1923. Must contain 15 % alc; blackcurrants macerated in neutral spirits/brandy for 2 months. First produced 1841.
Caymana	Ireland	Banana cream; 17 % alc.
Cédratine	Corsica	Sweet Lemon.
Cerassella	Italy	Cherry & Herbs from the Abruzzi mountains; red in color.
Chambord	France	Framboises (small black raspberries) and other fruits/herbs; contains honey. The 'Liqueur Royale de France'
Charleston Follies	France	Marie Brizard liqueur in chromed cocktail shaker package.
Chartreuse	France	130 herbs; distilled and blended in brandy with honey. Green (55 % alc.) and the sweeter Yellow (40 % alc). 200 g/L sugar. The yellow product contains orange and myrtle. Aged for two years before bottling. Made by monks at Voiron and Tarragona since 1605. 'Rediscovered' 1848.
Chéri-Suisse	Switzerland	Chocolate & Cherries.
Cherry Bestle	Denmark	Stevnsbaerret cherry.
Cherry Blossom	Japan	Pink cherry blossom liqueur.
Cherry Brandy	Various (EEC)	Distilled from juice of cherries; fermented with crushed cherrystones; some products are blended with Armagnac; red in color.
Cherry Heering	Denmark	Dark red cherry liqueur. 420 g/L sugar. Matured for 3 years. Produced for 170 years. (Orange, peach and blackcurrant Heerings also produced).
Cherry Marnier	France	Dalmatian cherries macerated in eau-de-vie. Red felt bottle.
Cherry Rocher	France	Cherry.
Cherry Whisky	Various	Whisky flavored with cherry. In Victorian times, known as 'gean'.
Cherry Gin	Various	Cherries in gin base.
Cherry Nalivka	Russia	Cherry.

Product/ Brand	*Origin*	*Description*
Chicoutai	Canada	Cloudberry.
Chocla Menthe	Netherlands	Peppermint & Chocolate
Chocolat Royal	France	18 % alc; Cocoa from Africa/S. America.
Chocolat Suisse	Switzerland	Chocolate.
Chokalu	Mexico	Chocolate.
Choya Umeshu	Japan	Japanese plum (*ume*) liqueur. Aged for 12 years.
CLOC	Denmark	Caraway; 31 % alc. Colorless. The name is an abbreviation of *cumin liquidum optimum castelli* ('the best caraway in the castles').
Cobana	Gran Canaria	Banana; bottle shaped like a bunch of bananas.
Cock O' The North	UK	Base on a recipe of the Gordon clan. Speyside malt whisky with blueberry and other flavors.
Coco Ribe		Coconut & Virgin Islands Rum; colorless; similar to Malibu.
Coffee Bestle	Denmark	Coffee
Cointreau	France	Orange; blend of sweet & bitter orange peel distillates/ macerates. 40 % alc; 250 g/L sugar; colorless. A French 'triple sec' Curaçao. Cointreau founded in 1849.
Coloma	Columbia	Coffee.
Congo	Holland	African liqueur; 22 % alc.
Cordial Campari	Italy	Cognac and raspberry; light yellow.
Cordial Médoc	France	Curaçao, Créme de Cacao and Cognac.
Cordial Reby	France	Cognac base; amber color.
Cream Liqueurs	Ireland/Various	Fresh Cream, spirits (Irish Whiskey; brandy; rum etc.) and flavorings (variants include mint, nuts, honey, whisky, coffee, chocolate, caramel, orange and peach). Bailey's is the leading brand. Others include Ashbourne, Myer's, Cadbury's, Heather, Chantré, Waterford, Carolans, Emmet's, Devonshire, Dubliner, O'Darby, St. Brendan's, Feeney's, Merry's, McCormick's, Terry's Chocolate etc. Also new range of niche category 'lite' creams, low in fat content for the 'calorie conscious' consumer (e.g. Bailey's Light; Creamlight etc.)
Crème de Alba	Spain	Brandy based cream liqueur
Crème d'Allash	France	Kummel.
Crème d'Amandes	France	Almond.
Crème d'Ananas	France	Pineapple; rum base.
Crème de Banane	France	Fresh ripe bananas; yellow color.
Crème des Barbades	France	Eau de vie flavored with cloves, cinnamon, mace and citrus peels.
Crème de Cacao	France	Cacao plus vanilla beans/spices. Rich deep chocolate flavor. Brown or colorless. 'Chouao' is the generic name for Venezuelan cacao beans.
Crème de Café	France	Coffee.
Crème de Cassis (de Dijon)	France (Dijon)	See Cassis.
Crème de Ciel	Netherlands	Like Curaçao; light blue color.
Crème de Fraises	France	Strawberry; red in color. *Crème de Fraises des Bois* is made with wild strawberries.

Product/ Brand	*Origin*	*Description*
Crème de Framboises	France	Raspberry.
Crème de Genièvre	France	Juniper Berries.
Crème de Grand Marnier	France	Cream Liqueur based on Grand Marnier.
Crème de Griotte	France	Morello cherry (sour, dark).
Crème de Guignolet	France	Cherry.
Crème de Kobai	Japan	Plum.
Crème de Mandarine (Mandarine de Blidah)	France	Tangerine or Blidah Tangerine.
Crème de Menthe	France	Mint/peppermint plus other herbs. Green or colorless.
Crème de Mirabelle	France	Plum.
Crème de Mocha (Mokka)	France	Coffee.
Crème de Mûre	France	Blackberry.
Crème de Myrtilles	France	Bilberry.
Crème de Noisettes	France	Hazelnuts.
Crème de Noix	France	Walnuts.
Crème de Noyau	France	Almond/Apricot kernels; colorless or pink in color.
Crème de Nuits	France	Blackcurrant.
Crème de Pecco	Netherlands	Tea flavored; colorless.
Crème de Peche de Vigne de Bourgogne	France	Small vine peach
Crème de Poire	France	Pear.
Crème de Prunelle	France	Plum; green in color.
Crème de Roses	France	Rose petals, citrus, vanilla; pink in color.
Crème de Thé	France	Tea.
Crème de Vanille	France	Vanilla beans.
Crème de Violettes	France	Violet and vanilla; pale violet color.
Crème des Barbades	France	Spices and Lemon peel.
Crème Yvette	USA	Parma violets. Named in honor of Yvette Gilbert . . . a French actress.
Cremibellota	Spain	Acorn flavored cream liqueur.
Cremocha	USA	Coffee.
Crystal Comfort	USA	Colorless version of Southern Comfort; 36 % alc.
Cuarante y Tres (Licor 43)	Spain	Made in Cartagena. Vanilla/citrus; contains 43 herbs/fruit. components. Yellow in color.
Curaçao	Various	Orange from peel of bittersweet 'green' oranges (*Citrus auruntium curassuviensis*), grown on island of Curaçao. Various color liqueurs (blue, green, orange, colorless etc.).
Cusenier Orange	France	Bittersweet orange distillates/ macerates.
Cynar	Italy	Quinine and Artichoke aperitif. Golden brown color. 18 % alc.
Damson Gin	UK	Dark red color.
Danzy Jones	Wales	Whisky liqueur. 40 % alc.
D'Avellans	Spain	Nut.
Della Notte	Italy	Black Sambuca.

Product/ Brand	*Origin*	*Description*
De Kuyper	Netherlands	Famous range of Dutch liqueurs and cordials including Cherry Brandy. (made from ripe cherries, kirsch, herbs and syrup); Blue Curaçao; Crème de Bananes; Crème de Cassis; Crème de Menthe; Apricot Brandy.
Der Lachs	Germany	The original aniseed and caraway liqueur with genuine 22 carat gold flakes.
Di Saronno Originale Amaretto	Italy	Almond & Apricot kernels steeped in alcohol. Created in 1525. Commercially produced since 18th century. 290 g/L sugar.
Dojon	France	Almond flavored cognac liqueur.
Domanier	Netherlands	Orange
Donauwalzer	Austria	Egg cream and milk liqueur.
Donjon	France	Almond flavored brandy liqueur.
Dooley's	UK	Toffee liqueur. Non-cream base.
Dr. McGillicuddy's	USA	Range of Schnapps brands (e.g. 'menthol mint').
Drambuie	Scotland	Prince Charles Edward Stuart's liqueur ('Bonnie Prince Charlie'). Scotch whisky plus herbs, heather honey and spices. The name originates from the Gaelic '*an dram buidheach*' meaning 'the drink that satisfies'. One of the oldest liqueurs (1745). 340 g/L sugar.
Drambuie Cream	Scotland	Lower fat cream liqueur, with malt whisky and heather honey.
Duchalet Chocolat Mousse	Switzerland	Swiss dark chocolate in a base of apple and pear schnapps. Old gold bottle; 20 % alc.
Dutch Delight	Netherlands	Chocolate, cream and vanilla.
Eau de Noix-Serres	France	Green walnuts/brandy.
Echte Kroatzbeere	Germany	Wild Blackberry; 30 % alc.
Edelweis	Italy	Alpine flower extracts from Moroni.
Elixir d'Amorique	France	Herbs.
Elixir d'Anvers	Belgium	Distilled from a blend of herbs, roots and fruits in a brandy base. Green or yellow (37 % alc.) (like Chartreuse). First produced 1863. Octagonal bottle.
Elixir di China	Italy	Anise.
Elixir dell'Eremita	Italy	Monastic herbal recipe.
Elixir de Garrus	France	Vanilla, saffron, maidenhead fern.
Elixir de Rotterdam	Netherlands	Herbs.
Elixir de Spa	Belgium	Brandy plus about 40 herbs. First produced 1858. Green 'drop-shaped' bottle. 40 % alc. Produced by Capuchin monks.
Elixir Vegetal (Chartreuse)	France	Herbs; 71 % alc; first produced 1737. Aged for 13 years minimum prior to bottling.
English Rose	UK	Cream liqueur with rose essence. Pale pink in color. 17 % alc.
Enzian	Bavaria	Mountain gentian.
Escarchado	Portugal	Anise; has sugar crystals in bottle.
Espresso	Italy	Coffee.
Ettaler	Germany	Herb base; yellow (42 % alc) and green (44 % alc).
Fantasia	Italy	Banana.

Product/ Brand	*Origin*	*Description*
Fernet Branca	Italy	Herbal wine-based digestif (bitters); contains 30 herbs/roots including camomile, saffron, gentian and rhubarb. First produced 1845.
Figaro (The)	Austria	Marzipan based cream liqueur with almond and sweet cherry.
Filfar	Cyprus	Herbs and orange.
Fine Sève	Canada	Maple syrup, eau de vie liqueur. Aged 3 years
Fine Pyrénées	France	Angelica.
Fior d'Alpi	Italy	Flowers and herbs from the Alps; twig and sugar crystals in bottle.
Forbidden Fruit	USA	Shaddock (grapefruit family) with honey and orange in a brandy base. Flame red in color; sweet with astringent aftertaste.
Fraise de Bois	France	Wild strawberries.
Fraisia	France	Strawberries; red in color.
Frangelico	Italy	Wild hazelnuts blended with berries, herbs and flowers. Formulation based on a 300-year-old recipe developed by a hermit in the Piedmont area of Northern Italy. Launched 1978. 'Monk' shaped bottle; 24 % alc.
Freezomint	France	Crème de Menthe from Cusenier. Green or white in color. Balloon shaped bottle.
Frigola	Balearic Islands	Thyme flavor.
Frostbite	Scotland	50 % alc. Strong mint flavor.
Fruyquina Aperitif Bourguignon	France	Aperitif from grape must, aromatic plants and cassis.
Galliano	Italy	40 herbs, roots and flowers, including lavender, anise, yarrow, musk, cinnamon and vanilla. Golden yellow color in characteristic tall bottle. Invented by Arturo Vaccari from Leghorn. Basic ingredient of 'Harvey Wallbanger' cocktail. 340 g/L sugar.
Gallwey's Irish Coffee	Ireland	Irish whiskey, herbs, honey and coffee; matured in oak casks.
Genepi	Italy	Gentian extract.
Ginger Lady	France	Ginger.
Glayva	Scotland	Scotch whisky, herbs and honey; similar to Drambuie.
Glen Mist	Scotland	Scotch whisky, herbs, spices and honey; Red seal (40 % alc); Gold seal (26 % alc).
Godet	Ireland	Belgian white chocolate liqueur with cognac.
Godfrey's	UK	Range of schnapps brands including coffee, butterscotch, peach, apple, lemon and cranberry. 20 % alc.
Godiva	USA	Chocolate (Seagram).
Goldkenn	Switzerland	Chocolate (Gold bar bottle).
Goldwasser	Germany	Herbs, roots, seeds, citrus peels (aniseed, caraway and orange); colorless with floating gold leaf (gold was traditionally thought to have curative properties). Original brand made by Der Lachs in 1598. Danziger is a leading brand from Poland.
Goldschläger	Switzerland	Cinnamon schnapps with gold leaf.

Product/ Brand	*Origin*	*Description*
Gorny Doubnyak	Russia	Ginger, angelica, galingale, clove and acorns.
Gran Cala	Italy	Triple orange.
Grand Cumberland	Australia	Passion fruit.
Grande Liqueur	France	Similar to Chartreuse; yellow and green.
Grand Marnier	France	Blend of fine Cognac with bitter orange distillates. Amber color. Cordon Rouge and Cordon Jaune (254 g/L sugar) varieties; Grand Marnier established in 1827 at Neauphle-le Château. Range also includes Cent Cinquantenaire; Centenaire and Marnier-Lapostolle.
Grano d'Oro	Spain	Date.
Green Tea	Japan	Matcha and Gyokuro teas macerated in brandy and neutral spirits.
Guignolet	France	Cherry brandy from small sour cherries and bittersweet cherries (Burlat Bigarreau).
Gyokuro Rikyu	Japan	Green tea.
Halb Schimmegespann	Germany	Half bitter/half sweet; herbs
Half-om-Half	Netherlands	Curaçao and orange bitters; red/brown color.
Halb und Halb	Germany	
Hallelujah	Israel	Brandy with Jaffa orange.
Heering	Denmark	Cherry Liqueur created in 1818. Made from Danish Steven's cherries. The stones are crushed to provide a hint of almond flavor. Matured 3 years in oak casks prior to blending. Formerly marketed as Peter Heering Cherry Brandy.
Heidebitt	Belgium	Herbal liqueur based on 'Hasseltse Brandewijn', with flavor from purple heather flowers; 40 % alc.
Herbsaint	USA	Anis based liqueur simulating absinthe. 45 % alc.
Herman Jansen	Netherlands	Range of liqueurs (cherry brandy, apricot brandy etc). Founded by Pieter Jansen 1777.
Herukka	Finland	Blackcurrant.
Himbeergeist	Germany	Raspberry.
Holunderbeerlikoer	Germany	Elderberry.
Honey Blonde	Denmark	Honey.
Hoppe	Netherlands	Orange bitters.
Hot Damn!	USA	Cinnamon.
Hot Irishman	Ireland	Coffee and Irish whiskey; 22 % alc.
Irish Mist	Ireland	Blend of whiskey, heather, clover, 12 other herbs and foxglove honey. Amber color.
Irish Moss	USA	Rye whiskey, Irish moss
Irish Velvet	Ireland	Irish Whiskey base; used for making Irish Coffee.
Isolabella	Italy	Herbs.
Izarra (Izzarra)	France	Distillation of flowers, plants and herbs with Armagnac, sugar syrup and Acacia honey; green (48 % alc) and yellow (35 % alc). 'Izarra' means 'star' in the Basque language. First produced 1835.
Jägermeister	Germany	Fifty-six roots herbs and fruits; dark red in color; 35 % alc.
Johann Strauss	Switzerland	Plum liqueur.
Johnnie Walker Liqueur	Scotland	Herby/smoky character in a Scotch whisky base.

Product/ Brand	*Origin*	*Description*
Kahlúa	Mexico	Coffee; dark brown color. Top selling coffee liqueur (Hiram Walker). 490 g/L sugar.
Kahlúa Royale Cream	USA	Cream version of the original liqueur.
Kakao mit Nuss	Germany	White chocolate & hazelnut.
Kamasutra	Germany	Ginseng with apricot and/or coconut
Kamok	France	Coffee; served hot or cold.
Kamora	USA	Coffee.
Karpi	Finland	Cranberry and other berries.
KēKē Beach	USA	Key lime cream liqueur
KēKē Beach	USA	'Key Lime pie with a hint of graham' cream liqueur. McCormick Distilling. 15 % alc.
Kenya Gold	Kenya	Kenyan Peaberry Coffee.
King's Ginger Liqueur	UK	Ginger root macerated in spirit.
Kingston Black	UK	Apple aperitif. Somerset cider brandy and Kingston Black apple juice.
Kirsberry	Denmark	Danish Cherry wine speciality; 17.5 % alc.
Kirsu Nalivka	Eastern Baltic	Sweet cherry.
Kitron	Greece	Distillate of lemon leaves and brandy.
Klareis	Germany	Black Forest liqueur.
Kloster Ettal	Germany	Herbs from Benedictine monastery near Oberammergau, which is famous for its Passion play. Green and yellow in color.
Kokomo		Tangerine & Pineapple.
Kola		Kola nuts, citrus peels, tonka beans and vanilla.
Krambambuli	Germany	Cherry, angelica and violet extracts.
Krupuik	Poland	Honey
Kümmel	Netherlands	Principally caraway with some anise, orris, fennel and cumin; minimum 35 % alc. Neutral spirit base originates from grain/potatoes; colourless. One of the oldest liqueurs with 'digestive' properties. Bols brand produced since 1575. Others include Wolfschmidt, Fockink, Mentzendorff and Nicholoff.
Kwai Feh (De Kuyper)	Netherlands	Lychee flavor; brand name means 'precious concubine'. 20 % alc.
La Grande Passion	France	Passion fruit in Armagnac base.
La Sénancole	France	Herbal base; yellow in color; originates from Cistercian abbey of Senanque in Provence.
La Tintaine	France	Anise base; sprig of fennel in each bottle.
Lakeland	UK	Scotch Whisky and caramel flavors; 20 % alc
Lakka	Finland	Arctic Cloudberry. Also known as Suomuurain.
Lapponia	Finland	Loganberry.
Lava	USA	Cinnamon schnapps; bright red color.
Lemoncello	Italy	Lemon liqueur produced by Toschi; 32 % alc.
Lemonello	Italy	Lemon liqueur from Averna; 30 % alc.
Lemonier	France	Lemon Peel.
Licor 43	Spain	See Cuarante y Tres.
Limoncē	Italy	Lemon. Also available as cream version.
Lindisfarne	UK	Scotch whisky, herbs and honey.
Liqueur d'Angélique	France	Angelica in a Cognac base.

Product/ Brand	*Origin*	*Description*
Liqueur des Moines	France	Liqueur of the Monks; herbs in fine spirit base.
Liqueur de Noix Vertes	France	Walnut.
Liqueur d'Or	France	Golden color with flakes of gold. Lemon flavor.
Liqueur Jaune/(Verte)	France	Similar to Chartreuse; yellow (green) in color.
Liqueur de Sapins	France	Pine needle extract.
Liqueur de Thé Vert	Holland	Green tea
Liqueur de Violette	France	Violet roots & leaves; purple in color.
Lochan Ora	UK	Scotch whisky, herbs and honey.
L'Orléane	Canada	Blackcurrant
Lune de Miel	Reunion	Rum cream with orchid/white vanilla flower; amethyst stone set into each bottle
Mad Monkey	Switzerland	Tequila/Lime liqueur; 18 % alc; 20 ml bottle.
Magma	UK	Cinnamon schnapps; peppery aftertaste. 24 % alc.
Malabari	India	Cardamom cream liqueur (Neera brand).
Malibu	Barbados/UK	Caribbean light rum liqueur with Coconut; distinctive white bottle. Launched 1981.
Mandarine	France	Tangerine.
Mandarine Napoléon	Belgium	Sicilian mandarines steeped in Cognac and French brandie with 21 botanicals. First produced 1892; 38 % alc; 240 g/L sugar.
Mandarinetto	Italy	Mediterranean tangerine.
Mandorla	Italy	Almond.
Mangalore	France	Pimento base, with cardamom and cinnamon. Red; 40 % alc.
Manzana Verde	France	Apple liqueur from Nuits Saint Georges. 18 % alc.
Maple	Canada	Maple syrup in brandy base.
Maraschino	Italy	Crushed Marasca cherries /kernels; colorless; min. 24 % alc. and 250 g/L invert sugar.
Marie Brizard	France	Range of traditional French liqueurs (Anisette, Curaçao, Melon Watermelon, and Apry); company established in 1755.
Marnique	Australia	Quince. Brandy base.
Mastic (Masticha)	Greece/Cyprus	Brandy base with Anise and cashew tree sap (gum mastic). Greek product from island of Chios.
Mazarin	France	Like Bénédictine; amber color.
Mei Kuei Lu Chiew	China	Rose flowers.
Melette	Italy	Anise.
Mélisse	France	White Chartreuse; last produced 1900.
Menthe Pastille	France	Mint.
Mentuccia (Centerbe)	Italy	Mint and 100 herbs from the Abruzzi mountains.
Mersin	Turkey	A type of Triple Sec with herbs.
Mesimarja	Finland	Arctic bramble (*Rubus arcticus*).
Metz 40	UK	40 % alc. Schnapps with a twist of citrus.
Midori	Japan	Suntory's Honeydew melon liqueur; green in color; 21 % alc; developed in Japan in 1964; launched in USA 1978.
Mille Fiori	Italy	Contains extracts from 1000 flowers. A type of Fior d'Alpi.
Minaki	Canada	Blueberry.
Mirabelle	France	Cherry.

Product/ Brand	*Origin*	*Description*
Mirage	UK	Citrus fruit flavors in a wine and vodka base; 14.9 % alc.
Mirto di Sardegna Rosso	Sardinia	Myrtle berry and herbs.
Mirtocē	Italy	Myrtle berry
Mistrà	Italy	Aniseed and herbs; 40–47 % alc.
Misty	UK	Yoghurt based tropical cocktail.
Mohola	Japan	Ripe mangoes.
Molinari	Italy	Leading brand of Sambuca.
Monastine Abbaye St Gratien	France	Pale yellow in color; similar to Chartreuse.
Monastique	South America	Similar to Bénédictine.
Monin Original	France	Distilled lime peels with spices; popular with American troops in France (1917)
Monte Aguila	Jamaica	Pimento (allspice) and cloves in a rum base.
Monte Teca	Mexico	Tequila base.
Monterez	UK	White wine, brandy, fruit juice; 17.5 % alc.
Mozart	Austria	Chocolate and nougat (original); gold globe-shaped bottle. Also White (white chocolate); Black (dark chocolate and vanilla).
Mus	Turkey	Banana.
Nabana	France	Banana.
Nezhinskaya Ryafina	Russia	Rowanberry.
Nocello	Italy	Walnut liqueur; 24 % alc; Toschi.
Nocino	Italy	Whole green walnut kernels (*Jugians regia*); min. 100 g/L invert sugar and 30 % alc.
Norwegian Punch	Norway	Made from a Batavian arrak base; 27 % alc.
Noyau (Rosé)	France	Peach and apricot kernels; white (and pink) in color.
Ocha	Japan	Green Tea.
Old Pulteney	Scotland	Based on old Pulteney Scotch Whisky.
OP	Sweden	Aquavit-based spirit with orange, peach and ginger.
Opal Nera	Italy	Black sambuca: star anise, elder flower and lemon peel. Black color is partly derived from the skin of elderberries.
Orange brandy	Various	Liqueur brandy flavored with orange extracts; amber color.
Oro di Mazetti	Italy	Liqueur from Mazzetti d'Altavilla
Otelo	Mexico	Lime liqueur from Veracruz
Ouzo	Greece	Aniseed (and usually fennel), together with mastic from an indigenous plant (*Pistacia lentiscus Chia*) from the island of Chios. Drier and stronger than anisette. Must contain maximum 50 g/L sugar and be distilled in traditional copper stills, of less than 1000 litres in capacity.
Oxygén	France/USA	Aniseed.
Paan	Netherlands	Betel leaf, herbs and spices. Based on an Indian recipe; 37.5 % alc.
Pacharán	Spain	Fruit spirit drink flavored with sloe (*Prunus spinosa L.*; min. 250 g fruit per litre pure alc.) in anis base. Pink/red in color. Leading brand is Zoco (Pernod Ricard).
Palo	Balearics	Thyme.
Parfait Amour	France Netherlands	Curaçao flavored with rosewater, citrus, vanilla, violet oils, and almond; highly scented. Pink and violet in color.

Product/ Brand	*Origin*	*Description*
Pasha	Turkey	Coffee.
Passione Nera	Italy	Black liquorice sambuca
Passoã	France	Passion fruit; coral colored; 20 % abv, from Cointreau
Pastis	France	Spirit flavored with liquorice root (*Glycyrrhiza glabra*); max. 100 g/L sugar.
Peach brandy	Various	Peach in a brandy base; amber in color.
Peachtree	Netherlands	Peach schnapps from De Kuyper; introduced 1984; similar to Archer's. The popular 'Fuzzy Navel' cocktail is Peach schnapps and orange juice.
Pêcher Mignon	France	Peach (from Underberg).
Peppermint Pastille	France	Mint; green in color.
Pernod	France	Star Anise, fennel, herbs (including camomile, coriander and veronica) and flavorings in a spirit base. Pernod contains less licorice than Ricard Pastis 51. Original product made in the 18th. century contained wormwood (c.f. absinthe).
Petite Liqueur	France	Cognac, sparkling wine and coffee; amber in color.
Peychaud's	USA	Aromatic bitters.
Pihlajanmarja	Finland	Rowanberry.
Pimento Dram	Jamaica	Green and ripe pimento berries steeped in rum; dark red in color.
Pimm's (No.1 Cup)	UK	Invented in the 1840s. A fruit and spice punch based on London Dry gin, popular in UK and 'Colonial' territories; originally 31.4 % alc; now 25 % alc.
Pimpeltjens	Netherlands	Taste of bitter oranges; Curaçao with herbs. Little is known about the formula.
Pineau des Charentes	France	Blend of fresh grape juice and Cognac (2:1) from the Charentes region; it has an Appellation Contrôlée. Typically 14.5 % alc.
Pippermint Get (GET 27)	France	Created in 1796 in Revel by the Get brothers; green or white in color. France's No. 2 liqueur from Bacardi-Martini.
Pisa	Italy	Nut liqueur; 22 % alc; Leaning bottle.
Pisang Ambon	Netherlands	Indonesian recipe of green banana, exotic fruits and herbs; 21 % alc; green in color.
Pomeranzen	Germany	Green oranges, made in the Baltic States. Favored by King Edward VII.
Ponche	Spain	Distilled sherry base flavored with orange peel, plums, raisins and vanilla; brown in color. Soto brand has a silver colored bottle.
Praline	USA	Vanilla and pecan nuts; based on a New Orleans speciality confection.
Premier (Bols)	Netherlands	Neutral spirit, Cognac, old genever, herbs and citrus peels. 40 % alc. Launched 1992.
Prunelle (de Bourgogne)	France	Sloes or plums; pale green in color.
Pucker	Netherlands	Grape Pucker and Cheri-Beri Pucker Schnapps from De Kuyper; 15 % alc; fruit and acid aftertaste.
Punchetta	UK	Liqueur rum with fruits.
Puschkin Black Sun	Germany	Black vodka liqueur:Wild fruits (forest berries)
Puschkin Red		Blood Orange/Herbs.

Product/ Brand	*Origin*	*Description*
Queen	Germany	From Behn Co. Marasca cherry with Scotch Whisky; Grapefruit with Jamaican rum; Peppermint with Chocolate.
R (Ór)	Ireland	22 % vol Irish schnapps. Fruit and botanical extracts.
Rabinowka	Eastern Europe	Rowanberry (mountain ash); dry and sweet varieties; pink or claret red in color.
Raki	Turkey	Aniseed and liquorice.
Raspail	France	Angelica, myrrh, calamus and other herbs; yellow in color. Has digestive properties; first produced 1847.
Ratafia	Various	Wine (or marc) spirit base flavored with almond, peach or cherry kernels.
Razzmatazz	Netherlands	Raspberry, from de Kuyper
Ricard	France	Anise and herbs; pastis.
Rock & Rye	N. America	Whiskey base flavored with fruits. Often contains crystals of rock candy or pieces of fruit.
Rohöl	USA import	Cinnamon, mint, herbs, juniper and chilli pepper. 35 % alc. Packaged in black oil drum.
Romana Sambuca	Italy	Elder flower and anise; originated in Civitavecchia. Traditionally served flaming in a glass with three coffee beans.
'Royal' Chocolate range	France	Various styles including orange, cherry, ginger, mint, French coffee, chocolate.
Rumpleminze	Germany	Peppermint schnapps; 50 % alc.
Rute Grütze	Germany	Raspberries, strawberries, raspberries, cherries and red currants.
Sabra	Israel	Jaffa orange and bitter chocolate; red in color. Name originates from Sabra Desert cactus.
Sacco	Italy	Peppermint.
Safari	Netherlands	African drink; exotic fruit (mango, papaya, maracuya, wild lemon-lime); 20 % alc.
St. Hallvard	Norway	Herbs in a potato spirit base; bright yellow in color.
Sakura Cherry Blossom	Japan	Cherry blossoms macerated in neutral spirit.
Sambuca	Italy	Colorless liqueur flavored with Anis (*Pimpinella anisum*), Star Anise (*Illicium verum*) and Elder flower (*Sambucus nigra*). Min. 350 g/L invert sugar and 38 % alc. Biggest selling liqueur category in Italy.
San Michele	Denmark	Tangerine.
San Silvestro (Mentuccia, Centerbe)	Italy	100 herbs; pale green in color.
Sapin d'Or	France (Jura)	Piney aroma; green in color. Produced in Pontarlier since 1825; similar to Bénédictine. Tree-shaped bottles.
Sazerac	USA	Bourbon based cocktail
Schnapps	Various European	Light and refreshing taste; wide range of flavors; currently in vogue; not as sweet as traditional liqueurs. Enjoyed with mixers (fruit juice, carbonates etc). See Archers, Rumpleminze etc.
Sevoco	France	Spices and cacao; light brown in color.
Sheridan's	Ireland	A unique double (2-bottle) liqueur; chocolate/coffee (26 % alc.) and vanilla/cream (17 % alc.). To make an alcoholic version of Irish Coffee.

Product/ Brand	*Origin*	*Description*
Silberwasser	Germany	Aniseed and orange. Colorless with flakes of silver. (c.f. Goldwasser).
Sidekick	UK	Cranberry, grapefruit, sour apple and vanilla schnapps drinks. Served in 30 ml 'shot pot,' designed to clip on side of beer glass.
Soho	UK	Lychee based; 24 % alc
Sloe Gin	UK	Sloe fruit (*Prunus spinosa*; blackthorn) macerated in gin. Tangy flavor like wild cherries. Deep red color.
Snowstorm	USA	Menthol wintergreen schnapps. Creates winter scene when bottle is inverted.
Solbaerrum	Denmark	Blackcurrant in rum base.
Sonnema Berenberg	Netherlands	Bitters based on Geneva gin flavored with 71 herbs and spices.
Sortilège	Canada	Berry liqueur
Sour Apple Pucker	Netherlands	Schnapps from de Kuyper
Sourz	UK	Apple flavored; 15 % alc. from JBB. Peach and pine-apple also produced
Southern Comfort	USA	Peach and Orange in a grain spirit base. Often perceived as a whiskey. 120 g/L sugar.
Stag's Breath	UK	The name originates from Compton McKenzie's book *Whisky Galore*. Scotch Whisky and honeycomb.
Starry Night	USA	Orange citrus
Stönsforder	Germany	Slightly bitter; dark in color.
Strega	Italy	Infusion of 70+ herbs in fruit spirit; light yellow in color due to saffron. Pot distilled and matured in wood. Strega means witch
Stroh Cream		Rum and alpine milk.
Suomuurain	Finland	Cloud berry.
Surfers	Netherlands	Range of low alcohol liqueurs (14.5 % alc.) e.g. 'Green Banana'.
Suze	France	Wine-based gentian bitters launched in 1889. 16 % alc.
Swedish Punsch	Sweden	Rum base, spicy taste; drunk hot or cold.
Taboo	UK	Wine and vodka blended with natural essences of peach, apricot and exotic fruits; 14.9 % alc.
Tamakari	Malta	Herbs.
Tangerine TTE	France	Tangerine; red in color.
Tangoa	UK	Tangerine and orange in cognac.
Tapio	Finland	Herbs and Juniper berries. Colorless.
Teichenné	Spain	Range of 13 schnapps brands including butterscotch, peach, melon, banana, kiwi and apple flavors.
Terry's Chocolate Orange	UK	Produced as a liqueur version of a famous confection.
Tia Maria	Jamaica	Blue Mountain coffee and spices in a cane spirit/rum base; dark brown in color. 340 g/L sugar.
Toussaint	Germany	*Coffee; 250 g/L sugar.
Trappistine	France	Herbs; pale yellow-green. Compounded with Armagnac from Abbey de la Grâce de Dieu, Doubs.

*Named after General Toussaint L'Ouverture, a hero of Haitian independence, declared in 1804.

Product/ Brand	*Origin*	*Description*
Très Bourbon	Reunion	Vanilla liqueur; bottle decorated in 22 carat gold.
Tres Castillos	Puerto Rico	Anise with sugar candy.
Triple Sec	Various	Orange liqueur like Curaçao, but drier and stronger. Made with blend of bittersweet 'green' Curaçao and sweet orange peels.
Tropico	USA	Bacardi Gold rum with exotic natural fruit juices.
Truffles	USA	White and Dark Chocolate.
Tuaca	Italy	Orange and vanilla in brandy base. 35 % alc. Golden yellow color.
Tuica	Romania	Plum.
Underberg	Switzerland	Herbal bitters; first produced 1846. Characteristic brown paper-wrapped miniature bottle. 44 % alc.
Unicum	Italy	Bitter liqueur digestif.
Utu	Denmark	Orange.
Van der Hum	South Africa	Made from the 'Naartje' (S. African tangerine) plus herbs, seeds, barks etc. macerated in grape spirit with sugar and glucose. 'Van der Hum' means 'what's his name' since no one could recall who invented the drink. First produced in 17th. century. A cream version is also produced.
Vandermint	Netherlands	Chocolate with a hint of mint.
Vanilchina	Italy	Quinine and vanilla aperitif.
VeraMint de Ricqlès	France	Mint.
Verveine du Vélay	France	Distilled from 33 herbs including verbena. Created in 1859; yellow or green (55 % alc.) in color. Based on Charentes brandy.
(La) Vieille Cure	France	50 herbs macerated in Armagnac and Cognac. Originates from an abbey at Cenon.
Villa Massa	Italy	Lemon liqueur from Sorrento; also mandarin, orange, walnut
Vishnyovaya Nalivka	Russia	Cherry.
Viva Lemon		White rum, tropical fruits and citrus.
Wallace Single Malt	Scotland	Named after William Wallace. 35 % alc; made with Scotch Malt whisky.
Wiener Walzer	Austria	Chocolate and grape in Cognac base.
Wild Turkey	USA	Herbs, spices and other flavors in a Bourbon base; amber color; 30 % alc.
Wildebraam	South Africa	Youngberry.
Wisniowka	Poland	Cherry.
Wolfschmidt	Netherlands	Brand of kümmel originating in Latvia.
Wurzelpeter	Germany	Herb.
Yukon Jack	Canada	Based on a blend of Canadian whiskies with citrus flavor. Introduced 1974. Often consumed as a 'shooter' with beer. The mixture is called a 'Grizzly'. Also Yukon Jack 'Perma Frost' Schnapps.
Zafaran	India	Zafaran and other herbs.
Zwack Unicum	Austria	Range of Viennese fruit liqueurs (pear, apricot, café etc.).

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15

Cachaça, Pisco and Tequila

J. B. Faria, Eduardo Loyola, Mercedes G. López and Jean Pierre Dufour

CACHAÇA: THE BRAZILIAN SUGAR CANE SPIRIT

Historical Background

The Brazilian sugar cane spirit, also called cachaça, caninha or pinga, is the oldest and most consumed spirit drink in Brazil, holding the brand world record production of distilled beverage in 1993 (Drinks International, 1994).

The Brazilian sugar cane spirit was first obtained by using the sugar cane waste, called "borra" from the cane sugar plants, which started its production in 1534. Little is known about when and where the Portuguese who lived in Brazil, first distilled the fermented "borra" to make cachaça, except that they probably began distilling it between 1543 and 1550, using their knowledge of "bagaceira" production.

The word cachaça may have its origin in the Iberian term "cachazza", which referred to a cheap beverage consumed in Portugal and Spain, or it may derive from the female of the pig "cachaço", probably because the hard meat of a wild pig from the Northeast region of Brazil was softened by the use of cachaça (Carvalho, 1988).

The production of cachaça was first intended for the slaves, but as time passed, more and more people began to drink this beverage, which stimulated producers to start fermenting the sugar cane juice. In the beginning of the 1600s cachaça and sugar were traded commercially all over the Northeast region of Brazil, and were also bartered for slaves by the Brazilian ships travelling to the African coast.

Until the end of the second World War, the cachaça industry was essentially rural comprised of a large number of small producers who planted sugar cane, made cachaça, and traded their own product. Some of them bottled their own products and a few would bottle cachaça from other producers. There was no deliberate aging process, however, due to its slow and low consumption, great amounts of spirit were kept in wooden casks for a long time, improving its sensory quality.

In the post war period, with the growth of the population and the incorporated habit of drinking cachaça, producers expanded their sugar cane plantations and also the production capacity of their distilleries. Small scale production gave way to large plants, with continuous distil-

lation and to large bottling companies, with their own commercial brands (Lima, 1983).

The estimate production of cachaça according to the Brazilian Beverages Association is about 1,3 billion litres a year, however considering the non official production by a great number of small distilleries spread throughout the country and the difficulties in controlling their production, the volume may be even higher.

Although in the beginning, the sugar cane spirit production was based in the sugar industry residue, nowadays most of the Brazilian sugar cane spirit is made from fermented sugar cane juice. The old regulations about the sugar cane spirits, after several changes in the past, were finally consolidated by the decree n° 2314 (Brazil, 1997), which defined the spirits made from fermented sugar cane juice by the terms "cachaça", "caninha", or "aguardente de cana". After that, the decree n°4072, reserved the term "cachaça" only for the sugar cane spirit made in the Brazilian territory, as well as the term "caipirinha", for the Brazilian lime drink made with "cachaça" (Brazil, 2002).

Cachaça Regulations

According to Brazilian legislation, "cachaça" is a distilled alcoholic beverage, that has 38 to 48 % alcohol v/v, at 20 °C, obtained by distilling fermented sugar cane juice, and may have the addition of not more than 6 g of sugar per litre, for taste correction. When the amount of sugar added is 6 g to 30 g per litre, the beverage is called "sweetened cachaça".

The congeners coefficient, also called secondary compounds or volatile impurities cannot be lower than 200 mg or higher than 650 mg for every 100 ml of pure ethanol, according to the following higher limits expressed in milligrams per 100 ml of pure ethanol:

volatile acidity (as acetic acid)	150
esters (as ethyl acetate)	200
aldehydes (as acetaldehyde)	30
furfural	5
higher alcohols	300

This beverage may have no more than 200 mg of methanol per 100 ml of pure ethanol and 5 mg of copper per litre. It can be called "aged cachaça", when it contains at least 50 % sugar cane spirit aged for a period not shorter than 1 year (Brazil, 1997).

Raw Material

The sugar cane (*Saccharum spp*) used to produce cachaça must be mature, be in good phytosanitary conditions, have been harvested recently, and not have experienced any kind of deterioration.

Sugar Cane Juice Extraction

The sugar cane juice is extracted by pressing the cane in several types of mills, that have different shapes and capacities, to provide, as a rule, the best economical extraction. From this choice will depend the overall plant productivity.

Small plants usually have only one simple mill with three axles, into which cane is fed by hand without any previous preparation.

Must Preparation

The extracted sugar cane juice is itself a natural must. To achieve better fermentation and more economic results, some procedures must be performed to reduce the initial contamination by micro-organisms, to obtain a more adequate sugar concentration, and to promote the action of yeast over that of other micro-organisms.

In addition adopting hygienic practices throughout all the industrial process, which includes the proper handling of raw material and the cleaning of all equipment that is in contact with the juice, some specific procedures are usually followed to prepare the juice for fermentation (Lima, 1983)

The first recommended treatment is to separate by gravity the broad and heavy impurities that are in the juice. Then, the juice usually must be diluted to adjust the sugar juice content and the fermentative yeast capacity, in order to avoid inhibition of yeast action, by higher alcohol levels. This practice reduces sugar losses and pre-

vents further bacterial fermentations that may occur after the normal process is finished.

Corrections of juice pH values from the normal 5,5 to 4,5 by adding sulphuric acid, and of the temperature to 30 °C are also made to favor yeast action.

Finally, disinfectants and antibiotics to eliminate undesirable micro-organisms as well minerals, vitamins and other nutritive materials may be added to preserve and support the fermentation process.

After these procedures, the juice, now called must, is ready for the alcoholic fermentation.

Fermentation

The sugar cane juice fermentation is a very robust process, that can occur even under technical adverse conditions, due to the higher adaptive capacity of the yeasts. This robustness may lead to the neglect of the fermentation process among several small producers, which causes unnecessary losses and lowers the sensory quality of their products.

The fermentation process should be conducted preferentially in specially built industrial areas, with maximum hygiene, good light and ventilation conditions and easy disposal of residues. The tanks for fermentation, and all the other equipment related to the fermentation process are normally put together in these areas.

The tanks used in the fermentation of cachaça are of different materials and shapes. The most commonly used are cylindrical tanks of carbon steel, which may be open or closed, with the height twice the diameter. For such tanks, it is also recommended the use of internal refrigeration with coils, but depending on the region and climate, some producers work without any kind of refrigeration or use external cooling system.

The volume of the fermentation tanks also varies widely, but it must be compatible with the capacity of the distillation equipment.

The Yeast

The choice of the yeast to be used will depend on the must preparation, the plant conditions and the desired characteristics of the final product.

The best yeast to produce a good cachaça are those isolated from fermenting sugar cane must and, if possible, from the same region. The use of selected yeasts is common in large distilleries, but this type of yeast cannot be used in plants lacking skilled technical personnel, proper hygienic conditions and adequate techniques.

Many small-scale production units still use bread-making yeasts, or the so called "fermento caipira", natural or wild yeast mixtures that are developed in the distilleries themselves or are based on empirical regional recipes (Lima, 1999).

The Fermentation Process

The alcoholic yeast fermentation stage is similar to that of many other beverages, and it begins just when the sugar cane must is put together with the yeasts.

In order to obtain a good fermentation the yeasts have to be previously multiplied to a mass or volume, high enough to conduct an efficient and economic fermentation process. Several successive small-scale fermentations, using increasingly volumes of must under adequate conditions and yeast concentration, are normally carried out to produce the initial yeast solution (Yokoya, 1995).

The fermentation process has three distinct phases: preliminary phase (4 hours), principal or turbulent phase (12–16 hours) and finishing phase (4-6 hours). At the beginning there is rapid cellular multiplication, small increase of temperature and low production of carbon dioxide. The principal phase is characterized by a high production of carbon dioxide and agitation, which are the visible effects of the high cellular activity. The density slows down as the temperature, the alcohol percentage and the acidity increase. In some cases it is necessary to refrigerate the tanks to lower the temperature. It is also very common in this phase the appearance of a broad, viscous and voluminous foam, with quite different features from place to place.

Finally, in the finishing phase the production of carbon dioxide decreases and the temperature is lowered as all sugar is consumed.

In the cachaça industry, the fermentation may be conducted by discontinuous or continuous

processes. Most distilleries employ a discontinuous process which reuses the yeast cells. In the most common process, after ending a fermentation, the fermented material is left standing to allow the solid mass of yeast cell to be separated by gravity. Then, the wine is sent to be distilled and the residue called "pé-de-cuba" (10 to 20 % of the volume), after treated, receives the new must for the next fermentation. Some plants also separate the wine by centrifugation, send the supernatant to be distilled and treat the remaining cream with water, sulphuric acid (pH = 2.2–3.2) and shaken for 4 h. Finally the cream is sent back to the tank for a new fermentation. In both cases the initial phase of the fermentation is very reduced, and the higher concentrations of yeasts (3×10^6 cells/ml), help reaching the turbulent phase in a shorter time, reducing the fermentation time and bacterial action.

Given the practices in handling the raw material and the non-sterilization of the juice, there is a frequent risk of infection all through the process. This risk is even higher in the small-scale distilleries, where any kind of microbiological laboratory control is almost impossible. In such cases it is possible to detect and sometimes prevent possible fermentation problems by attending to the following observations (Lima, 1983; Yokoya, 1995).

- The fermentation time is 24–30 hours: variations on this time under similar conditions during the crop period are not expected, and must be evaluated.
- The normal fermentation of sugar cane produces a good fruity aroma. The presence of new undesirable odors may indicate a contamination problem.
- The foam of sugar cane fermentation depends on several factors and is quite distinct, changes in its appearance during the crop period are not normal.
- Changes in the temperature curves during the crop period may also indicate some kind of fermentation defect.
- During the fermentation process, the density of the must decreases in a harmonic way, so changes observed in its pattern may be due to temperature variations or contamination.
- Usually, great changes in acidity during the fermentation are not expected, consequently final values of acidity higher than twice the initial value are not normal.
- Finally, the most visible warning of bacterial contamination is the appearance of *Drosophila,* the vinegar fly, in the fermentation areas. It is an indication of acetic infection and of its extent, which is proportional to the number of flies.

Sugar Cane Wine Composition

After fermentation, the must is called wine and may have a variable composition of gaseous, solid and liquid compounds.

The carbon dioxide present in small quantities in the wine is the main gaseous component. The solid components are yeasts cells, bacteria, mineral salts, non fermented sugars and other impurities.

From a quantitative point of view, water and ethanol are the most important liquids in the wine (from 88:12 to 93:7), but also present, in smaller quantities, are secondary products, minor components that are very important for distillate quality. These by products of the alcoholic fermentation and of the action of contaminant micro-organisms include acids, aldehydes, esters, ketones, glycerol, fat acids, nitrogen compounds, higher alcohols and other components.

Distillation

The wine is distilled to separate and concentrate the distilled compounds from the residual components, which will be discarded.

Cachaça distilleries use discontinuous, semi-continuous or continuous systems. The spirits from the first two distillation systems, also called batch distillation process, have quite different composition and sensorial quality than those from the continuous system.

Discontinuous and Semi-Continuous Systems

The discontinuous and semi-continuous systems, or batch distillation, are carried on in one,

two or three simple alembic or pot stills (Figure 15–1), usually constructed in copper, stainless steel, or using both materials.

The use of stainless steel distilling equipment to avoid copper contamination, produced a low quality cachaça, which pointed out an unknown and positive effect of the copper in the sensorial quality of cachaça. Efforts were made to eliminate copper contamination without producing the defect observed in cachaça distilled in absence of copper (Faria, 1982; Faria and Pourchet-Campos, 1989), and to learn more about the influence of copper in the quality of cachaça (Faria and Lourenço, 1990; Bettin *et al.*, 2002). The use of a copper insert in the ascending parts of the stainless steel distillers was also proposed as a means to eliminating the copper contamination of the spirits, without causing the sensory defect observed when no copper was used (Faria, 1982; Faria, 1989).

In the discontinuous system, a simple distillation process gradually separates the compounds based on their volatility. The more volatile compounds, such as methanol and acetaldehyde, are distilled first in the head fraction, and the low volatile compounds, such as higher alcohols, are distilled later in the heart and tail fractions. The most important part of the distilling spirits is the intermediate "heart fraction" which is rich in ethanol and contain a lower quantity of impurities, term which are referred to all the substances that are distilled with the water-ethanol mixture. Cachaça produced using this system of distillation must have only the heart fraction, which is about 80–85 % of the total volume. In some cases, however the head and tail fractions are not entirely separated out.

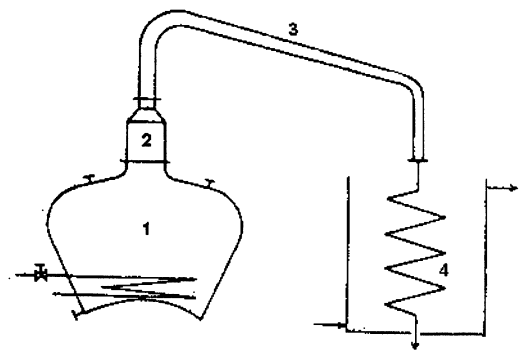


Figure 15–1 Schematic alembic or pot still used to produce cachaça. 1, kettle or *cucurbita*; 2, head or *capitel*; 3, condenser tube or *alonga*; 4, coil cooler or *serpentina* (Stupiello, 1992, p. 73).

The use of two or three pot stills in series improves the selectivity of the distilling process and represents a step towards the continuous system. Some different types of alembics used to produce cachaça are showed in Figures 15–2, 15–3 and 15–4. A process involving two distillation steps using the same alembic for distilling cachaça was also proposed to obtain a distillate of light aroma and taste to be further aged in oak casks for at least 2 years (Novaes, 1999; Bizelli, 2000).

Continuous Distillation

In the continuous distillation process columns fed with wine and vapor continuously produce the distillate as well as a residue called bad wine.

Inside the columns are plates with bubble-caps and siphon tubs that function as a series of single distillation apparatus. Each plate distils vapors through the bubble-cap of the next higher plate and receives the condensed liquid from that plate, through the siphon tub. Other types of column devices are used, but given the particular characteristics of the sugar cane the bubble-caps are the best suited, mainly because they are cleaner and more selective.

From the base, the vapor goes up to the top heating the plates, and distilling and separating mixtures which are increasingly richer in volatile components.

Figure 15–5 shows the classical system of continuous distillation used to produce cachaça. In this case the wine is fed near the top, and the bad wine is eliminated in the base.

In these columns the head products can be separated by the degassing condenser B_1 to obtain a more pure distillate. The tail impurities are partially eliminated with the bad wine.

One can summarize the role of distillation for all types of process, by noting that at this stage quality characteristics are added to the

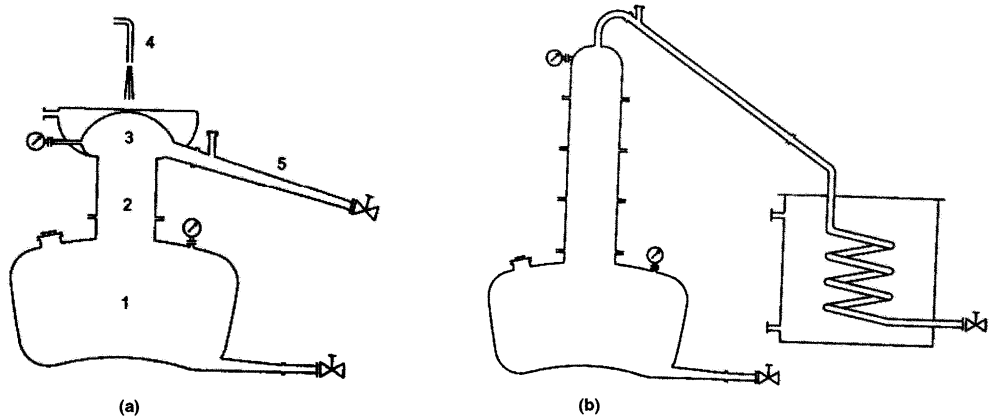


Figure 15–2 Some variations in cachaça alembic shapes. The "elephant head" type (a) and the "hot head" type (b) alembics. 1, kettle; 2, column; 3, head; 4, head cooler; 5, condenser tube; 6, coil cooler (Ribeiro, 1997, p. 36 and 37).

products by removing water and other volatiles (Stupiello, 1992). From this point of view, the best choice of a distillation system depends on the yield expected and the desired product characteristics.

Batch distillation has some important advantages over the continuous process. The easy elimination of the head and tail fractions and the richer aroma produced during batch distillation should be considered. In fact, the richer aroma of the cachaças distilled in alembics is related not only to the concentration changes that occur in the distillation process, but also to the chemical reactions that occur among the components in contact with the hot alembics walls (Cole and Noble, 1995). These reactions are also favored by the presence of copper and by the direct heating, normally used in this type of distilling.

The main advantages of continuous distillation are: greater distilling selectivity, increase in production, energy savings, decrease in undesirable sensory defects and standardization of distillate (Stupiello, 1992).

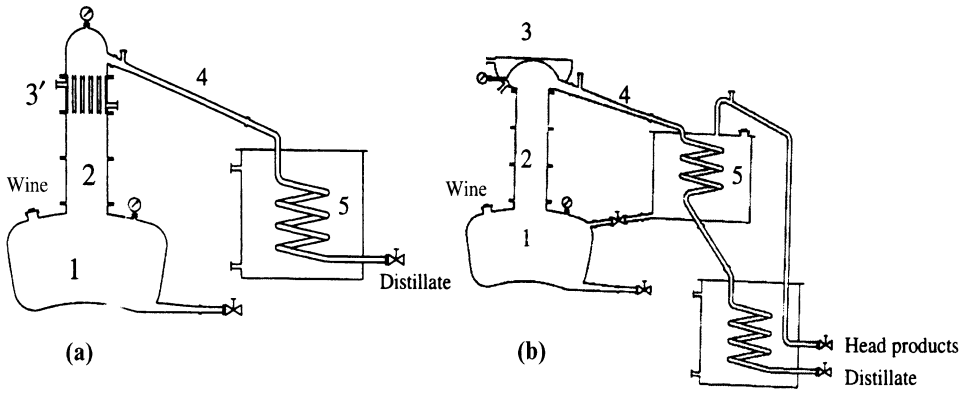


Figure 15–3 Some modified alembics. a, alembic with modified head cooler and coil cooler; b, alembic with head cooler; wine preheater and coil cooler. 1, kettle; 2, column; 3, head cooler 3′, modified head cooler; 4, condenser tubes; 5, coil cooler; 5′, heating wine coil (Ribeiro, 1997, p. 41 and 42).

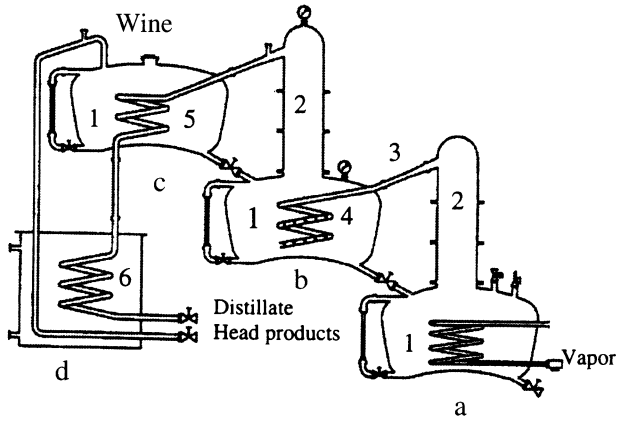


Figure 15–4 A semicontinuous distillation system with three alembics. 1, kettle; 2, column; 3, condenser tubes; 4, bored coil; 5, wine heating coil; 6, coil cooler (Ribeiro, 1997, p. 44).

Distillate Composition

The distillation process separates the volatile compounds from the wine yielding spirits for direct consumption, or higher alcoholic distillates with 54–95 % ethanol v.v., at 20 °C, to be used in the production of cachaça or other alcoholic beverages.

Table 15–1 shows the most common minor components of Brazilian cachaça and their concentrations.

Aging

Very few spirits have as good a sensory quality just after distilled as Brazilian cachaça has. Perhaps that is why the aging of cachaça is not a normal practice in Brazil, although this process produces a significant improvement in its flavor quality.

Only a small number of studies of the aging of cachaça have been carried out, but all of them show clearly the positive effect of aging on its sensory quality. Sensory evaluation of samples of cachaça collected during aging in oak casks showed a significant increase in flavor acceptability after 21 and 37 months of aging (Faria *et al.*, 1995).

The sensory profile of "cachaça" also showed significant changes during the aging period (Figure 15–6). After 48 months the aged product developed pronounced woody aroma, initial sweetness, sweet aftertaste, vanilla aroma, yellow coloration, initial woody flavor and wood flavor aftertaste. The alcohol aroma, aggressivity, initial alcohol flavor and alcohol flavor aftertaste of the aged sample, were significantly lower than those of the other samples (Cardello & Faria, 1998; Cardello & Faria, 2000).

The development of good characteristics from the oak, and the loss of the harsh characteristics of the new distillate as seen in whisky aging (Reazin, 1983; Canaway, 1983) were also observed in the cachaça during aging. Results of a time intensity analysis of samples of cachaça aged in oak casks for 48 months (Figure 15–7) show clearly the development of sweetness and wood taste and the decrease of alcoholic taste and aggressivity, as a result of the aging process (Cardello and Faria, 1999).

Oak is the best preferred wood for the aging of cachaça, probably because the well-known characteristics of oak aged whisky and cognac had made these the patterns of good quality aged beverages. Given the great number of Brazilian wood species, studies were conducted using several distinct kinds of wood to determine whether aging in other types of wood might have similar good effects on cachaça. Interesting results were obtained with: amendoim (*Pterogyne nitens*) (Almeida *et al.*, 1947); cabreuva (*Myroscylon*

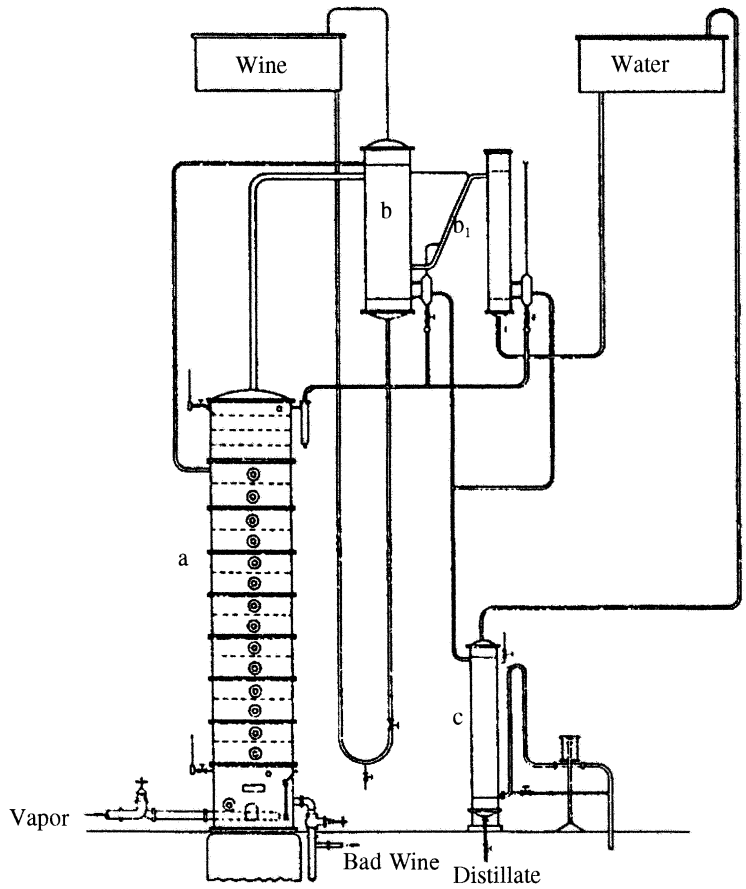


Figure 15–5 Scheme of a classic distiller used to produce cachaça. a, column; b and b_1, vertical condensers; c, cooler coil (Stupiello, 1992, p. 77).

peruifum) (Lima, 1974) and freijó (*Cordia goeldiana*) (Cavalcanti *et al.*, 1978); as well as with amendoim (*Pterogyne nitens*) and pereiro (*Aspidoesperma pyrifolium*) (Bôscolo, 1996).

Very good reasons exist to include the aging as part of the production process for cachaça in order to improve its quality. Unfortunately, the majority of Brazilian producers, supported by government regulations, prefer to add sugar instead of aging their spirits.

Some Aspects Related to Quality of Cachaça

The Brazilian cachaça industry is so vast, with so many small and large distilleries, that it is very difficult to describe its negative aspects, without giving the idea that they are present in every production plant. In many industries, some of the problems which will be mentioned here may have never existed or have already been corrected.

Sulphur Compounds and the Sensorial Quality of Cachaça

The lower sensory quality of cachaça distilled in the absence of copper was first associated with higher sulphur contents (Faria *et al.*, 1993), and more recently has been related directly to the presence of dimethyl sulfide (DMS), which present in concentrations higher than 4.0–5.0 mg/L, may cause the characteristic sulfury sensory defect (Faria, 2000).

Table 15–1 Minor volatile components of young Brazilian cachaça

	Compounds	*Average*	*Standard deviation*	*Minimum*	*Maximum*
Acids[a]	Acetic acid	78.98	79.65	7.16	419
	Propionic acid	0.17	0.12	0.05	0.71
	Isobutyric acid	0.07	0.05	n.d.	0.28
	Butyric acid	0.14	0.15	n.d.	0.69
	Isovaleric acid	0.15	0.15	n.d.	0.53
	Valeric acid	0.04	0.06	n.d.	0.25
	Isocaproic acid	0.03	0.03	n.d.	0.15
	Caproic acid	0.22	0.19	n.d.	0.69
	Heptanoic acid	0.06	0.18	n.d.	1.25
	Caprilic acid	1.29	1.06	0.02	4.14
	Capric acid	1.65	1.27	0.26	6.89
	Lauric acid	0.63	0.41	0.21	2.25
	Myristic acid	0.36	0.24	n.d.	1.51
	Palmitic acid	0.56	0.98	n.d.	7.01
Alcohols[b]	Methanol	5.66	2.24	0.87	9.20
	Amyl alcohol	0.13	0.04	0.05	0.20
	1,4-Butanodiol	0.13	0.05	0.04	0.20
	n-Butanol	1.15	0.02	0.90	1.62
	Cetyl alcohol	6.13	2.43	2.20	10.10
	Cynamic alcohol	6.95	1.94	3.50	12.00
	Decanol	0.21	0.17	n.d.	0.60
	n-Dodecanol	0.01	0.01	n.d.	0.05
	Geraniol	0.62	0.17	0.25	0.86
	Isoamyl alcohol	138.00	26.00	13.00	198.00
	Isobutanol	62.00	14.00	40.00	96.00
	Menthol	0.51	0.13	0.25	0.73
	2-phenilethyl alcohol	0.02	0.03	n.d.	0.09
	n-Propanol	46.00	7.00	37.00	60.00
	n-Tetradecanol	0.04	0.05	n.d.	0.17
Aldehydes[c]	Formaldehyde	0.19	0.21	0.002	1.20
	Hydroxymethylfurfural	0.49	0.40	n.d.	1.86
	Acetaldehyde	11.20	3.91	3.30	20.00
	Acrolein	0.14	0.15	n.d.	0.66
	Furfural	0.40	0.55	n.d.	2.60
	Propionaldehyde	0.02	0.01	n.d.	0.06
	Butyraldehyde	0.20	0.31	n.d.	1.90
	Benzaldehyde	0.13	0.13	n.d.	0.54
	Isovaleraldehyde	0.06	0.06	n.d.	0.21
	Valeraldehyde	0.11	0.06	n.d.	0.31
Esters[b]	Amyl propionate	0.02	0.01	n.d.	0.03
	Ethyl acetate	23.80	7.30	12.60	39.00
	Ethyl benzoate	0.46	0.20	0.13	0.84
	Ethyl heptanoate	0.05	0.01	0.03	0.09
	Isoamyl valerate	0.01	0.01	n.d.	0.02
	Methyl propionate	0.02	0.01	n.d.	0.05
	Propyl butyrate	0.02	0.01	n.d.	0.05
Sulfur compounds[d] (mg/l)	Dimethyl sulfide	4.96	2.23	1.15	7.94

Results given as mg/100 ml pure alcohol unless otherwise indicated; n.d., not detected.

[a]Data from Nascimento *et al.* (1998).

[b]Data from Bôscolo *et al.* (2000).

[c]Data from Nascimento et al. (1997).

[d]Data from Faria (2000).

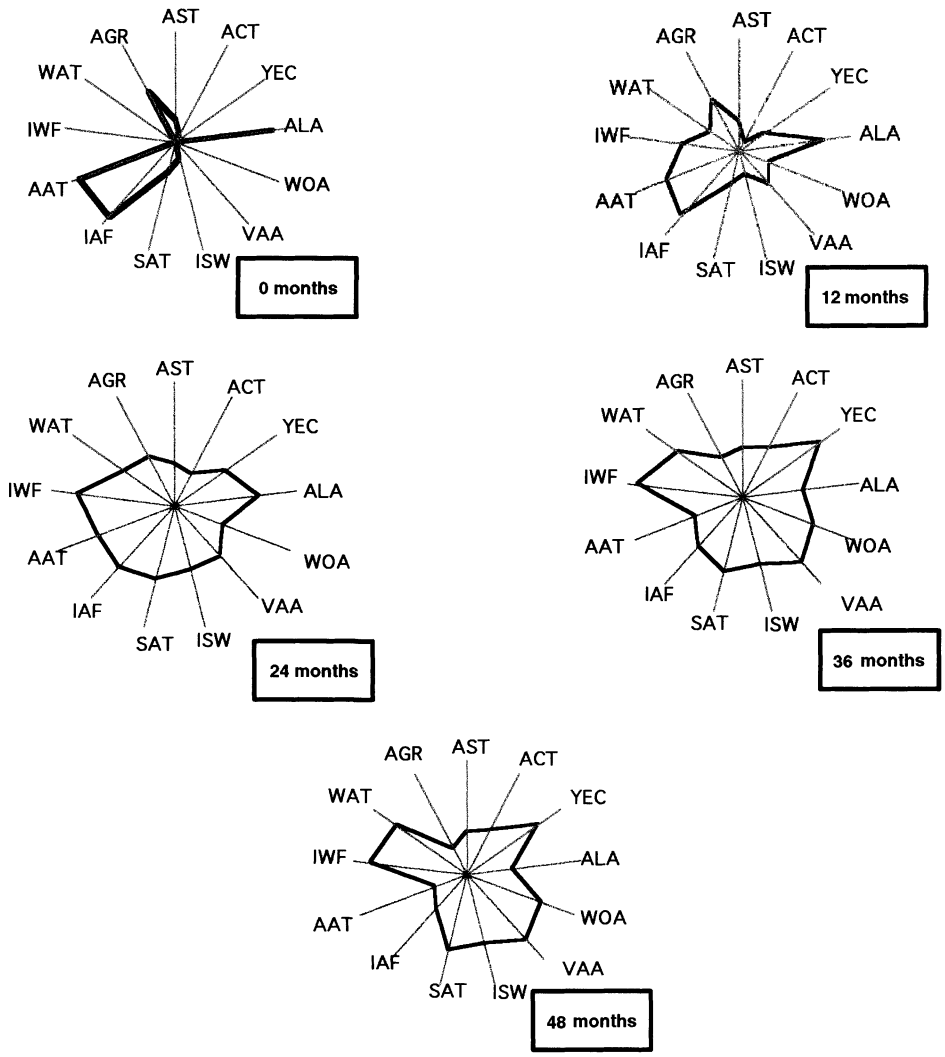


Figure 15–6 Spider-web graph of sensory attributes of cachaça aging in oak casks during 4 years: AST, astringency; ACT, acid taste; YEC, yellow coloration; ALA, alcoholic aroma; WOA, wood aroma; VAA, vanilla aroma; ISW, initial sweetness; SAT, sweet aftertaste; IAF, initial alcoholic flavor; AAT, alcoholic aftertaste; IWF, initial wood flavor; WAT, wood aftertaste; AGR, aggressivity (Cardello & Faria, 1998).

As already mentioned, the use of copper in the ascending parts of stainless steel distillation apparatus may solve this sensory problem and avoid the copper contamination (Faria, 1982; Faria & Pourchet-Campos, 1989). The aging process can also reduce or eliminate this sensory defect (Isique *et al.*, 2001).

Inappropriate Handling and Industrial Practices

Some common and erroneous practices adopted by the cachaça industry have a direct effect on the quality of cachaça.

It is very common before harvesting, to burn the cane to remove the leaves. This anti ecological practice which adds ash to the juice and a burnt

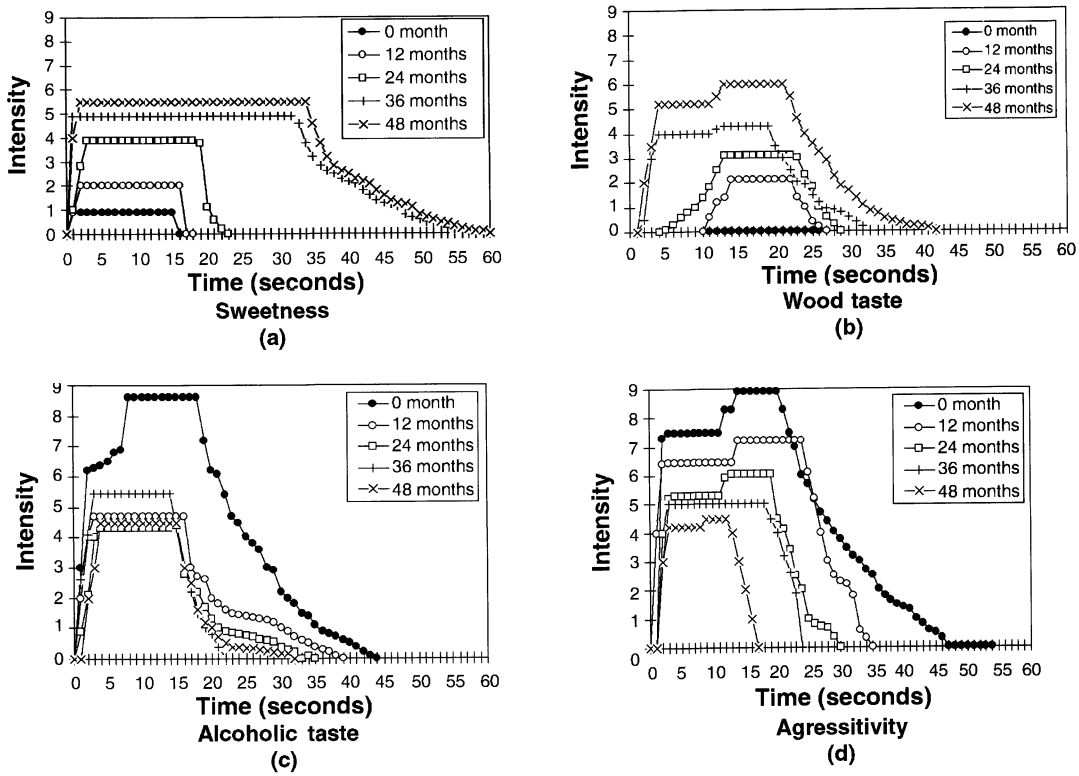


Figure 15–7 Time-intensity analysis of sweetness (a), wood taste (b), alcoholic taste (c), and agressivity (d) in cachaça samples aging during 4 years (Cardello & Faria, 1999).

taste to the spirits (Ribeiro, 1997), also promotes microbiological contamination, mainly because the cane sugar exudation comes in contact with dirt and other impurities after the harvest.

The lubricant oils used in the mills may also contaminate the juice during extraction or during direct injection of the vapor used to move the mills into the distilling columns. The same type of petroleum derivative compounds may also contaminate the spirits, when the latter are stored in tanks lined with asphalt. This means of storing cachaça is common practice in some cachaça plants.

The lack of skilled professionals to assist in the distilling process is also a cause of occasional or frequent deviation from normal and correct distillation practices. The attempt to generate yields higher than the nominal capacity of the distillation equipment is a very common error, that certainly affects the quality of the distillate. The columns are designed to separate selectively the volatiles expected to constitute the distillate when appropriate techniques are used. The use of higher volumes of wine to increase production and the need for more vapor may disrupt the normal balance of the apparatus, drawing with the expected vapors other foreign and undesirable compounds (Novaes, 1992). Similar problems may occur with the alembics when the operator tries to increase the production volume, collecting more distillate or speeding up the distillation process. This will certainly change the composition and affect the quality of the distillate.

Modifications or new design for the distillation apparatus that clearly affect the composition of the spirits and their quality, are also very commonly seen.

Sugar Addition and Legal Regulations

As previously mentioned, the possibility of adding up to 3 % of sugar in the sweeten cachaça has led several producers to follow this practice instead of trying to improve the sensory quality of the cachaça by technological innovation. This way of masking the sensory defects, which is not recommended for the quality and the image of the spirit, is also related to another technological problem of cachaça; the formation of haze or flocks, due to the late precipitation of commercial sugar dextran with other distillate components after bottling. This defect, which impairs the visual appearance of alcoholic beverages, may have some distinct origin (Sielberg, 1999), but in cachaça it is related mainly to the addition of sugar (Isique, 1999).

New Detected Contamination

Two new problems related to the production of cachaça should be mentioned here: the presence of ethyl carbamate (Boscolo, 1998; Farah Nagato *et al.*, 2000) and polycyclic aromatic hydrocarbon compounds (Bettin, 1999).

Ethyl carbamate occurs naturally in alcoholic beverages at low ppb levels. Because is a non volatile compound, when it is formed before the distillation process, it does not appear in the distillate but its precursors may distil with the spirit and cause latter contamination by this compound.

As mentioned earlier, besides the possibility of contamination of the juice during its extraction by the lubricant oil of the mill and of the must by the direct injection of the mill vapor escape in the distillation columns, the storage of the spirits in tanks coated with asphalt, as well to burn the cane before harvesting may cause the appearance of polycyclic aromatic hydrocarbon compounds in the cachaça (Bettin, 2001).

These two undesirable contaminations are certainly promoted if the cachaça distilling process is carried out faster than the distillation called for by apparatus specifications.

Cachaça Production and Market

Although Brazilian cachaça has a great potential for export, most of its production has been directed to the internal market, where the competition is based mainly on the price of the product. In many cases, increases in profit have been linked primarily to quantity, not quality.

Although prejudices still exist about drinking cachaça, the consumption of good quality cachaça is growing in Brazil, however the low international market price is still not attractive for good quality products (Ribeiro, 1997).

To change this situation efforts have been made to improve the quality of cachaça and to develop real conditions for its export. The activities of producers associations like ABRABE (Brazilian Beverages Association) and AMPAQ (Quality Spirit Producers Association of Minas Gerais State), involving technical and research areas, have already been showed their good effects on the improvement of the quality of Brazilian cachaça.

Conclusions

Cachaça is the most consumed spirit in Brazil and also the third most produced all over the world. Just after distillation, it has a very good aroma and flavor that may become even better by aging in wooden casks.

The excellence of several cachaça brands is responsible for the growing internal consumption of good quality cachaça, as well the Government efforts to promote the cachaça exportation are also showing good results. In the last year Brazil exported near 11 millions litres of cachaça and is planning to reach 30 millions litres at the end of this decade.

The improvement of the cachaça quality joining together producers, research institutions and Government, is certainly the best way to recognize the historical social and economic importance of this Brazilian beverage, and to profit from its exportation.

PISCO

Introduction

Pisco is a distilled alcoholic beverage obtained from wine. Its most distinctive feature is that it is mainly obtained from varieties that have a strong

flavor. It is not aged in wood therefore it is colorless. In the last few years, however, there has been a tendency to add a touch of wood but this is so slight that it does not affect the flavor of the grapes.

Pisco is produced in several countries of the Andean zone of South America. Its main producers are Chile and Perú who have maintained a longstanding discussion of its origin. Nevertheless, it is in Chile where in the last few years there has been a significant increase in its production and a relevant change in the technology applied to produce it, that is why we will describe the process and the main characteristics of this beverage.

Production Zone

Production of Pisco in Chile is delimited to a zone which according to legislation is an Origen Denomination. This zone comprises five valleys that are named after the rivers that form them. These valleys run from the Pacific Ocean to the Andes mountain, therefore are constantly increasing altitude respect of sea level. This means that the cloudiness, temperature and luminosity is modified as it goes up from the coast to the Andes.

The varieties of grapes that can be used to ellaborate pisco are also defined by the ruling of origin denomination which includes 13 varieties, the majority belong to the Muscat group and are the following:

Chasselas Musque Vrai
Yellow Muscat
Early white Muscat
Muscat of Alexandria or Italia
Muscat of Austria
Muscat of Frontignan
Muscat of Hamburgo
Black Muscat
Pink Muscat
Moscato Canelli
Orange Muscat
Pedro Jiménez
Torontel.

Out of these 13 varieties only 5 cover most of the vineyards planted for production of pisco. The absolute and relative area respect of the total of vineyards devoted to pisco is shown on Table 15–2.

The main features for these varieties according to Pszczolkowski and Bordeu, 1981; Hernandez and Pszczolkowski, 1986; Hernandez and Kyling, 1987 are the following:

Muscat of Alexandria, also known as Italia, is typical for its large, loose, cilindric clusters with large matt green eliptic grapes which turn brownish as they ripen. Its main feature is its intense flavor. The resulting wine is alcoholic and very aromatic and its spirits are of great quality.

Pink Muscat has large cone shaped clusters rather loose and with different grades of Shot berrie (millerandage). These grapes are pink, eliptic and large. The grapes and the wine have a strong flavor of which a great quality alcohol is obtained.

Yellow Torontel or Torrentes Riojano (Alcalde, 1989) has large cylindrical clusters

Table 15–2 Principal varieties of grape used to produce pisco and planted area

Varieties	*Planted area (Hectares)*	*Relative area (%)*
Muscat of Alexandria	1,700	16.7
Pink Muscat	2,525	24.8
Torontel	858	8.4
Muscat of Austria	2,440	23.9
Pedro Jiménez	2,384	23.4
Others accepted	280	2.7
Total	10,187	100

From Servicio Agrícola y Ganadero [Ministry of Agriculture], Chile.

with irregular grapes takes a golden color as they ripen. Although it is a late variety it produces a medium alcoholic degree wine, with a high pH and low acidity. It has a typical strong fragrance and its quality is considered good for pisco.

Pedro Jiménez (Alcalde 1989) has large loose cylindrical clusters with medium sized round yellow green grapes, very sweet and juicy but they are flavorless. It is mainly a rustic, coarse variety with high production. Its wines are very alcoholic (15 to 16 GL). Azócar (1991) found low contents of terpenics (under 0,09 mg/l in Pedro Jiménez wines which confirms that this variety is flavorless.

Muscat of Austria are cone shaped clusters, compact of large grapes and little pruine, greenish that turns golden as it ripens. They are flavorless and slightly moscatel. It is a precocious variety that produces abundant and even crops. It is vastly planted in the pisco zone in Chile. The wine is flavorless to mildly moscatel it produces an acceptable quality of alcohol and it is easy to mix.

Out of the five varieties that production is based upon only three have outstanding features for the production of pisco and two of them contribute very poorly to the fragrance that should be present in this beverage.

Due to the important surface covered by varieties that do not have aromatic features, studies have been carried out to introduce varieties of better aromatic qualities and also of a better yield (Bulnes, 1988; Ibacache, 1994) have established that Early Muscat and Yellow Moscatel are the most aromatic with a larger amount of free and bounded terpenes (Agosin *et al.*,1995). M Alexandria and M Rosada have the same amount of free terpenes but M Alexandria has a larger amount of bounded terpenes. The main terpenes of Muscat of Alexandria are geraniol and nerol and in the case of Pink Muscat the main terpene is linalool (Agosin *et al.*, 1994; Bordeu *et al.*, 1994).

Harvest season begins at the end of February to May, and even may extend to early June. The picking of the grapes will be determined by the Probable Alcohol Degree (P.A.D.) this will depend upon the variety, location of the vineyard and the system used to conduct the grapevines (Pszczolkowski and Kyling, 1987; Pszczolkowski. 1997).

The effect of the different varieties in determining the ripeness has been widely discussed. Valenzuela (1978) concludes that to obtain the best combination of flavor and taste, ripeness should be 14.8 GL for Muscat of Alexandria, 13.2 GL for Pink Muscat, 16 GL for Muscat of Austria.

Espinosa (1981) on the contrary maintains that the optimum ripeness for the Muscat varieties fluctuates between 11.5 °–12 ° P.A.D. (Espinosa, 1981).

The influence of the production areas becomes clear when ripeness is compared between the areas close to the coast and the inner valleys, where over ripened grapes are often found with 14 °–16 ° P.A.D. Sectors with coast influence can produce grapes with insufficient ripeness (Gallegos, 1992; Pszczolkowski, 1997). This difference in the concentration of sugar in grapes has determined that reception plants have predefined ranges of tolerance for its concentration. Currently, the minimum and maximum ranges of P.A.D. required by the vinification plants are 11.5 ° and 14 ° GL, respectively.

Conduction systems that provide the cluster with a luminous and warm microclimate contribute to a better relation between solid solubles/acidity and ethanol/acidity both in grapes and wine. These relations allow for a better sensorial evaluation of wines used to elaborate pisco (Ferrada, 1992; Gallegos, 1992; Pino, 1993; Egaña, 1994; Valenzuela, 1996).

Vinification in the Pisco Industry

Vinification of grapes to make pisco, permanently seeks to transfer to wine an important part of the aroma of moscatel grapes which is its main feature. In order to achieve this, grapes used to be processed in contact with skin, thus allowing its maceration during the fermentation process. This was changed some ten years ago as it caused more problems than advantages. These problems were related to the excesive extraction

of polyphenols, extraction of herbal flavors and a difficulty in controlling temperature which produced losses of ethanol and flavors.

Currently obtaining flavors from skins is done through a prefermentation at 14–18 °C from 12 to 24 hours. Under these conditions, migration of phenols to a liquid phase is low.

Alcoholic fermentation is usually done with selected strain of yeast of the *Saccaromyces cerevisiae* species and in some cases yeasts that reveal flavors are used, but not always successfully.

Temperature control is one of the worst problems affecting vinification in the pisco zone, this control depends on the type of container used. Up until ten years ago most of the fermentation tanks were made of epoxicated cement which proved difficult to cool. In recent years the use of stainless steel tanks has become more common as these are cooled from the outside with a water shower. In both cases fermentations are made under different temperatures. In the case of cement tanks the temperature is 30 degrees and in stainless steel tanks it is around 22 °C.

The inconveniences of fermenting at high temperatures are several:

a) Violent alcoholic fermentations
b) Flavor loss
c) Larger loss of alcohol
d) Sluggish fermentation
e) Wines with a high concentration of reducing sugars.

Fermentation temperatures determine that the process will last between 4 to 6 days. In general it is advised that the fermentation should be made in closed stainless steel tanks to obtain an anaerobic atmosphere to prevent to some extent the loss of volatile compounds.

The conservation of wines is difficult as in some cases there are some remaining residual grams of sugar and the use of sulfur dioxide should be limited to small dosis. The use of this antiseptic was banned in the first regulations relative to pisco because if applied before the fermentation it mixes with acetaldehyde and during destilation this bound breaks resulting in that a great amount of the aldhehyde remains in the spirit (Bordeau and Pszczolkowski, 1982).

The maximum amount recommended to prevent deterioration of the spirit is 5 g/hL (Borja, 1985) but this level of concentration does not guarantee the microbiologic stability especially in wines of low acidity. It is therefore better to try the distillation as close as possible to the end of the alcoholic fermentation, but this is only possible with a low percentage of wines.

A practice that helps to preserve wines and that is generally used in the industry is to mix them with the non potable phase of the distillation. The mixture of wines with a 10 % of these distillates allows for the increase of wine degree up to 14 to 15 GL. Obtaining thus, their microbiological stability without damaging the quality of the spirit.

Distillation

In the particular case of pisco the aim is to obtain a flavored spirit produced from genuine wines.

The Origen Denomination legislation does not define the type of distillery or a unique procedure for the distillation of wines (Bordeu and Pszczolkowski, 1982) due to this it is possible to find distilleries that have different designs; the majority are discontinuous.

All the alambic stills are made of copper as this metal is an excellent heat conductor, it is not affected by the wine acids, it fixes traces of H_2S and has the capacity of saponifying the different fatty acids of the wine (butanoic, haxanoic, octanoic decanoic dodecanoic) of disagreeable smells, forming neutral insoluble soaps. The use of copper is indispensable as it eliminates negative compounds in the spirits (Bordeau and Pszczolkowski, 1982).

It is recommended to have special care when cleaning the alambic still to ensure that no soaps or remainings are left as this would prevent direct contact of wine and the copper (Pszczolkowski and Bordeu, 1981; Bordeu and Pszczolkowski 1982; Pszczolkowski and Kyling, 1987).

The type of alambic still that best adapts to the pisco zone corresponds to one shown on Figure 15–8.

Boiler: recipient where the wine is boiled. When the boiler is steam heated, the steam is conducted by an inner coil.

Hat: It is the most important part of the equipment it works as a partial condenser of vapors that the boiler emits. The grade of condensation obtained determines to a great extent the quality of the spirit. In the pisco alembic stills it is possible to find various types of hats that have different ways of refrigeration. Some have a passive system that exchanges heat with the surrounding air, others are refrigerated by water. In the last few years, tubular condensers are being used to obtain greater efficiency and are easier to clean.

Preheater: A pot with the same capacity as the boiler that has an inner tube that carriers the non condensed vapors in the hat, its function is to preheat the wine that will be put into the boiler in the following batch, thus saving time and energy.

Condenser: This is a total condenser that ought to transform all the vapors into liquid of a temperature below 15 °C. In both cases it has the shape of a coil or a group of parallel pipes both refrigerated externally by water.

Rectifying column: This is a small plate column (6 to 8 plates) in which the alcoholic degree is raised. This column is only used in a phase of the distillation, in the pisco industry it is normal to use it when the alcoholic degree of the spirit is 30 degrees. Only some equipment has them and its objective is to save energy and time.

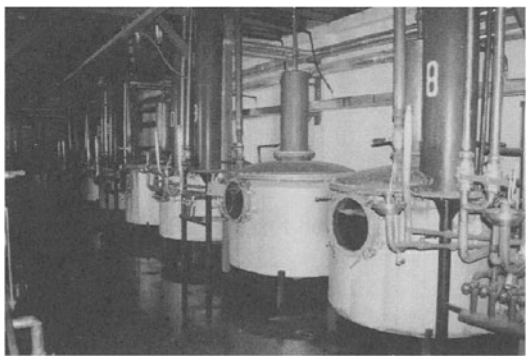


Figure 15–8 Pot stills characteristic of pisco zone.

Distillation Method

As expressed before classic distillation is discontinuous and has only one batch (a premier jet). In this type of distillation the three phases are separated in one batch of the alembic still obtaining "head", "heart" and "tail". The potable fraction is represented by the heart and the other two fractions are named "impures", these fractions are mixed and are redistilled mixed with the wine to recover ethanol and other compounds of interest to the spirit.

A standard distillation process (Quezada, 1973; Ureta *et al.*, 1986) to obtain pisco must consider:

Head: This first phase of distillation represents the first 10 to 20 minutes of the operation.

Heart: Is the fraction of the distillation that represents the potable alcohol. The way to obtain it is to proceed to a slow distillation just after the head fraction takes place until the resulting alcohol reaches 30 degrees GL.

Tail: This last fraction goes from the end of the heart fraction until the resulting effluent reaches 10 ° GL.

From this standard procedure variations are made depending on the composition of wine and if they are mixed with "impures". Modification of the processes are normally decided upon once the resulting spirit is tasted.

The potable spirit obtained immediately after distillation is not adequate for consumption because its volatile compounds are not harmonized and have not been combined that is why a maturity period is required (Pszczolkowski and Kyling, 1987). This period takes from 2 to 4 months in Rauli cooperage. This wood is ideal as it presents the necessary porosity to allow the alcohol micro-oxygenation, facilitating the complex combinations that improves alcohol quality. After the maturity period the alcoholic strength is reduced with demineralized water to avoid

cloudiness. The alcoholic strength depends on the type of pisco. Currently pisco is bottled under different alcoholic degrees which receive the following denominations: Selection 30 °GL, Special 35 °GL (it is the most popular), Reserved 40 °GL and Great Pisco 43 °GL.

If pisco presents suspended matters its fining is done with egg albumin and finally filtered through pad filters.

Chemical Composition of Pisco

Origin Denomination regulation establishes some dispositions about the composition of spirits, most of them related to the potability of the product, although in some cases they have been established to prevent its alteration.

The regulation refers to the single content of the majority congeners and additionally regulations on the minimum and maximum global contents are established (in g/l) :

Acids	1.50
Aldehydes	1.00
Methanol	1.50
Furfural	0.080

Apart from the dispositions related to the congeners above mentioned its total content is regulated. This should be over 3.0 g/L expressed in pure ethanol. Sugar content cannot exceed 5 g/L. There is no established requirement for fusel oils (propanol, isobutanol, 2- and 3-methyl-1-butanols).

Methanol contents are largely affected by skin maceration levels. When vinification was done by fermentative maceration the content was higher that one gram per litre and sometimes it was higher than the permitted concentration.

When the vinification without fermentative maceration became common practice methanol concentrations fell drastically to between 200 and 600 mg/L (Loyola, 1995).

Aldehydes: This compounds distils partially around one third of the initial content of wine and there is a possible transformation of aldehydes into other compounds which would be greater if a column were used (Ureta *et al.*, 1986). Aldehydes can be considered as head compounds even if they distil during the whole process (Pszczolkowski and Kyling, 1987). The content of aldehydes would be greater if the distillation is speeded (Conrads, 1988).

The main aldehyde contained in pisco is the acetaldehyde that can reach an 80 % of total aldehydes (Loyola *et al.*, 1990).

Acids: Acids distil from the beginning of the process and they increase gradually during distillation that is why they are considered tail compounds. Isobutyric and decanoic acids on the other hand are distilled in the heart (Ureta *et al.*, 1986; Pszczolkowski, 1977).

Esters: Are head compounds although they distil during the whole process of the distillation (Ureta *et al.*, 1986). The main factor that affects the content of esters is its concentration in wine that at the same time affects the functions of the fermentation conditions. Volatile esters contribute to enhance the aroma, as they provide floral and fruit aroma to spirit (Soles *et al.*, 1982), the most abundant ester in spirits is ethyl acetate which represents more than 52 % of esters contained in Pisco. This ester is in turn a negative component as it is responsible for a vinegar flavor (Migone, 1986).

Fusel Oils: In the pisco distillation fusel oils can be considered as head compounds and using the columns they increase in the heart fraction (Migone, 1986; Ureta *et al.*, 1986). There are certain differences in the time in which certain types of fusel oils distil (Ureta *et al.*, 1986). The normal concentration ranges of fusel oils in Pisco are 1.8 to 3 g/L at 100 °GL (Loyola & Herraiz, 1992; Migone, 1986).

Furfural: This aldehyde is formed mainly during the distillation of wine that have a high pentoses content. Its distillation begins at the middle of the heart and increases towards the tail (Espinosa, 1981; Ureta *et al.*, 1986. Furfural contents have decreased as the alembic still heating process has been changed. Currently steam heating allows for more even heat, thus avoiding spot overheating which affect the concentration of this compound in an important degree.

With regard to the minor compounds, there are no regulations and studies reflect a wide variation that depends on multiple factors amongst which the variety of grapes, alcoholic richness and distillation are some.

A study carried out (Loyola *et al.*, 1987) shows that samples of different valleys and spirits of different alcoholic degree had the following results.

Table 15–3 shows the wide variability of composition present in spirits which undoubtedly have different sensory responses, these differences are reduced in commercial products by blends that are determined by each firm's tasting panels.

It is necessary to enhance the wide variation observed in the terpenic compounds which give the spirit the moscatel character. This indicates that there is a different aromatic intensity in spirit which needs to be standardized by blend procedures.

A series of volatile fraction compounds have been identified in Pisco, which can affect aroma notably. Aroma is defined by terpenic compounds provided by the grapes and by secondary compounds provided by alcoholic fermentation. Relations between these compounds can be complex as interactions have been established that in many cases are hypo-additive indicating that the

Table 15–3 Concentration of various compounds in pisco

	Mean	*Maximum*	*Minimum*
Acetaldehyde	26.1	93.7	6.5
Ethyl acetate	240.6	851.8	50.4
Diethyl acetal	43.0	200.0	0.0
Methanol	925.0	2,231.1	117.1
1-Propanol	200.4	337.6	110.0
Isobutanol	416.0	586.6	287.4
3-Methyl-1-butanol	1,426.0	1,833.7	812.6
2-Methyl-1-butanol	343.0	535.4	213.8
Isoamyl acetate	1.2	5.4	0.1
Ethyl hexanoate	1.1	3.2	0.3
1-hexanol	4.9	10.8	2.6
Cis-3-hexen-1-ol	0.8	2.4	0.0
Furfuraldehyde	3.5	8.4	1.1
Ethyl octanoate	1.2	2.1	0.5
Benzaldehyde	0.1	0.2	0.0
Diethyl succinate	14.9	38.0	0.6
Ethyl decanoate	1.1	2.9	0.2
Isoamyl lactate	06	1.5	0.01
2-Phenylethyl acetate	1.3	3.1	0.4
Benzyl alcohol	0.5	1.1	0.1
2-Phenyletanol	20.7	55.4	2.3
Ethyl laurate	0.5	1.3	0.01
Linalool	4.1	9.0	0.8
α-Terpineol	2.6	5.6	0.6
Citronellol	0.5	1.2	0.2
Nerol	0.2	0.4	0.2
Geraniol	1.7	3.4	0.5
Hotrienol	12.39	0.0	29.13

Values are in mg/l of anhydrous ethanol.

different components of flavor are not additive but partially inhibit each other (Loyola *et al.*, 1987).

Flavor provided by moscatel grapes corresponds to terpenes distilled in the first fraction of the distillation. In hotrienol and α-terpineol an important distillation is observed in the heart fraction that might be due to the fact that these compounds are formed during distillation by high temperature (Loyola *et al.*, 1987; Loyola *et al.*, 1990; Ureta *et al.*, 1986).

According to another study carried out by (Rojas, 1984), total terpenic concentration in Pisco varies from 14.2 to 20.5 mg/L at 100 °GL.

Production and Consumption

In the last two decades production of pisco has increased importantly, reaching a maximum in 1995 (Table 15–4) which from there on started to decrease importantly. Currently there is an equilibrium between production and consumption.

Currently, the industry is facing overproduction which has been favored by imports of other alcoholic spirits. This becomes evident as from 1995 when production falls importantly. Fortunately this downfall has coincided with the increase in wine exports which has allowed for an important part of the wines that would have been destined to pisco is now left to cover internal wine needs.

When analyzing the consumption of alcoholic beverages in Chile it is concluded that 4.41 liters of alcohol expressed in 100 °GL per capita are consumed. Of this, pisco has a 0,76 L/ethanol in 100 °GL having a third place and only overcome by wine with 2,19 L and beer with 1,02 L of ethanol in 100 °GL (SAG 1999).

Pisco is almost only consumed within Chile as only 1 % is exported. Its consumption could increase internationally as it is well accepted by foreigners that visit Chile, specially when prepared as "pisco sour" which is made with pisco lemon and sugar.

To be able to successfully penetrate distilled alcoholic beverages in highly competitive foreign markets, a more aggressive marketing strategy should be implemented specially investing in marketing and publicity.

TEQUILA

Introduction

Tequila is a unique alcoholic beverage, which tradition, legacy and mythology dates back to pre-Hispanic times. The only raw material permitted for the elaboration of Tequila is one of the Agave families, specifically *Agave tequilana* Weber var. Azul. The word tequila comes from to nahuatl words: *tequitl*, that means work, position or duty; and *tlan*, that means place. Therefore, the name of this alcoholic beverage is given by its origin place: Tequila, Jalisco. In the Nuttall codex it is mentioned that Mayahuel the goddess of fertility, gave the nahuas all the things they needed to survive when she was converted into a

Table 15–4 National production of pisco

Year	*Thousands of bottles (665 ml) 30 °GL*	*Thousands of liters 100 °GL*
1975	12.151	2.430
1980	21.047	4.208
1985	27.155	5.430
1990	45.389	9.076
1995	70.165	14.033
1999	57.698	11.522

From Servicio Agrícola y Ganadero.

maguey (agave´s common name). Mayahuel as the Venus of Ephesus, had four-hundred breasts to feed her four-hundred children, the Centzon Totchtin (Muría).

On the other hand, the word agave means "noble" or "admirable" in Greek and was described by the first time by Linneaus in 1753.

Even though *Agave tequilana* is not exclusive to México, the production of tequila in Mexico is regulated by the Tequila Regulatory Council (CRT) formed in 1991 and whose main functions are to verify and certify that all Tequilas complied with the Official Mexican Standard ("Norma Official Mexicana (NOM)"), which controls the growing area and the plants which can be used. The norm also stipulates that only two categories of tequila are permitted: "100 % tequila of agave" and tequila. The second category allows the addition of 49 % of other fermentable sugars during the fermentation process. There are three types of Tequilas: Blanco (white), Reposado (rested) and Añejo (aged), these can be either a 100 % agave or mixed.

The elaboration, consumption and exportation of this beverage have a high relevance in Mexico, not only economically but also culturally. The production of tequila in Mexico from 1988 to 1998 went from 73,6 to 169,8 millions of liters (Figure 15–9). In 1998 more than 50 % of the annual production of tequila was exported to more than 80 countries. United States is the primary exporter with about 66 % follow by Netherlands, United Kingdom, Belgium, Japan, Brazil, Chile and France (Altesor, 1996).

Tequila is a relatively new alcoholic beverage in the European Community, however, it is still undergoing changes. The estimated forecast sales of Tequila for 1998 was of 1.4 million litres in Europe (Euromonitor).

Tequila is certainly one of the most recognized Mexican icons not only nationally but internationally.

Other Mexican alcoholic beverages less known abroad at the present time are mezcal (*Agave angustifolia, A. potatorum* and *A. karwinski*), pulque (*A. salmiana, A. atrovirens* and *A. mapisaga*), sotol (*Agave spp.*) and bacanora (*Agave spp.*) (Cedeño, 1995; Valenzuela Zapata, 2003). These beverages are made out of Agave

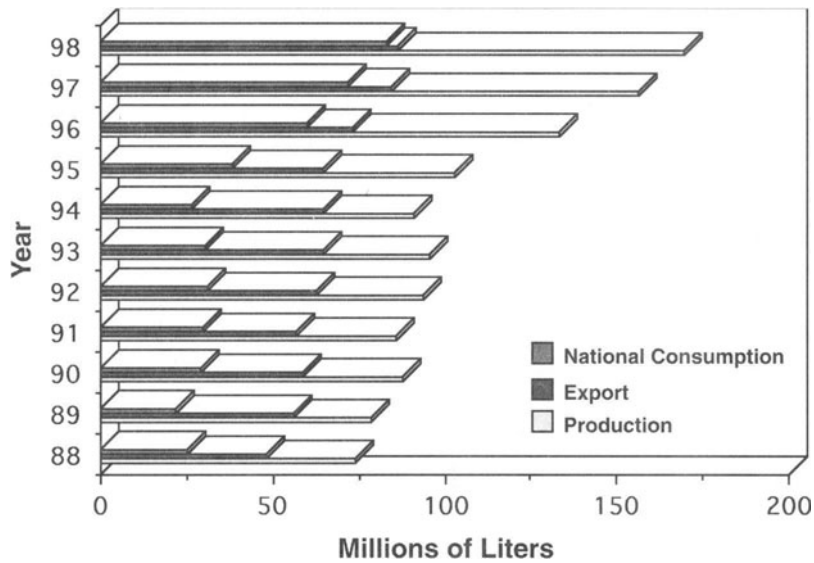


Figure 15–9 The Growth of the tequila industry.

plants too. It is believed that these will get in the international market very soon.

Materials

The Official Mexican Standard (NOM) for the Tequila production specified that only *Agave tequilana* Weber var. Azul (blue variety) can be used for its elaboration.

This same NOM also establishes that the beverage should not exceed the levels of the constituents listed in Table 15–5.

Besides, *Agave tequilana* cultivation is restricted to five geographic zones in México. The permitted regions are the states of Jalisco, Guanajuato, Nayarit, Michoacán and Tamaulipas. Agave plants must be between 7 and 9 years of age to be "Jimadas" (harvested). It is at this age that they have reached a significant level of fermentable carbohydrates.

As many other Agave plants, the pine or head of *A. tequilana* is highly rich in carbohydrates, specifically inulin (Table 15–6). Inulin is an oligosaccharide that belong to the fructans, β(1–2)fructofuranosyl linked to a terminal glucose unit. The exact degree of polymerization of inulin in agave is not known, however, NMR studies suggest that it should at least contain 20 units of fructose (data from López's laboratory). It has been published that the largest degree of polymerization does not usually exceed 30–35 units. *Agave tequilana* is known as the CAM (Crassulacean acid metabolism) plant which productivity per ground area is the highest of all this type of plants.

In spite of the many limitation to use only *Agave tequilana* Weber var. Azul for the production of Tequila, two types of the beverage can be made one is known as 100 % Agave if only *Agave tequilana* was used as a carbohydrate source and a mixed tequila which should have at least 51 % of *A. tequilana* the rest of fermentable carbohydrate could come from any other sugar sources cane, molasses, corn, to mention some.

Tequila Elaboration

Figure 15–10 shows the general steps involved during Tequila production.

Harvesting, Cooking and Mashing

The first step on Tequila production begins with the harvesting of *Agave tequilana* plants, this step is specifically known as "Jima". In general, Agave plants must be between 7 and 9 years of age before harvesting (Cedeño, 1995). It is believed that at these ages they have reach their minimum maturity therefore an important inulin content. At this point the pines weight between 20 to 60 Kg, they are transported to the distilleries, cut in halves and cooked in brick ovens for 36 hours at approximately 100 °C, during

Table 15–5 Levels of congeners in tequila

	Blanco		*Reposado*		*Añejo*	
	Min	*Max*	*Min*	*Max*	*Min*	*Max*
Percentage alcohol at 20 °C	38	55	38	55	38	55
Dry extract (g/l)	0	0.2	0	5	0	5
Higher alcohols	20	400	20	400	20	400
Methanol	30	300	30	300	30	300
Aldehydes	0	40	0	40	0	40
Esters	2	270	2	360	2	360
Furfural	0	1	0	1	0	1

From Valenzuela Zapata (1994).

Table 15–6 Chemical composition of *Agave tequilana*

	Azul	*Azul 2*
Water	62.00	60.00
Protein	0.02	0.02
Fiber	11.80	11.00
Inulin	20.01	24.00
Reducing sugars	1.03	1.50
Ash	2.50	2.70
pH	5.5	4.5

From Sánchez-Marroquín & Hope (1953).

this time a juice, known as agave juice, is collected and sent to the fermentable tank. After the 36 h, the ovens are cooled down, the pines are taken off, transported to a mashing machine and pressed to collect the rest of the agave juice, which is mixed with the one collected from the ovens. If the tequila is going to be a 100 % the fermentation step starts. However, if the tequila is going to be a mixed type, then a 49 % of other fermentable sugars is added in the tank.

The cooking step has been monitor to follow the type and quantity of compounds generated during this time. Collection of the agave juice exudates from a Tequila company were analyzed by GC-MS to learn about these compounds.

Among compounds present in the agave juice were 5-hydroxymethylfurfural (5-HMF), methyl-2-furoate, furfuryl alcohol, 2(5H)-furanone, 5-acetoxymethyl-2-furfural, 3,5-dihydroxy-2-methyl-4(H)-pyran-4-one (DMP) and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-

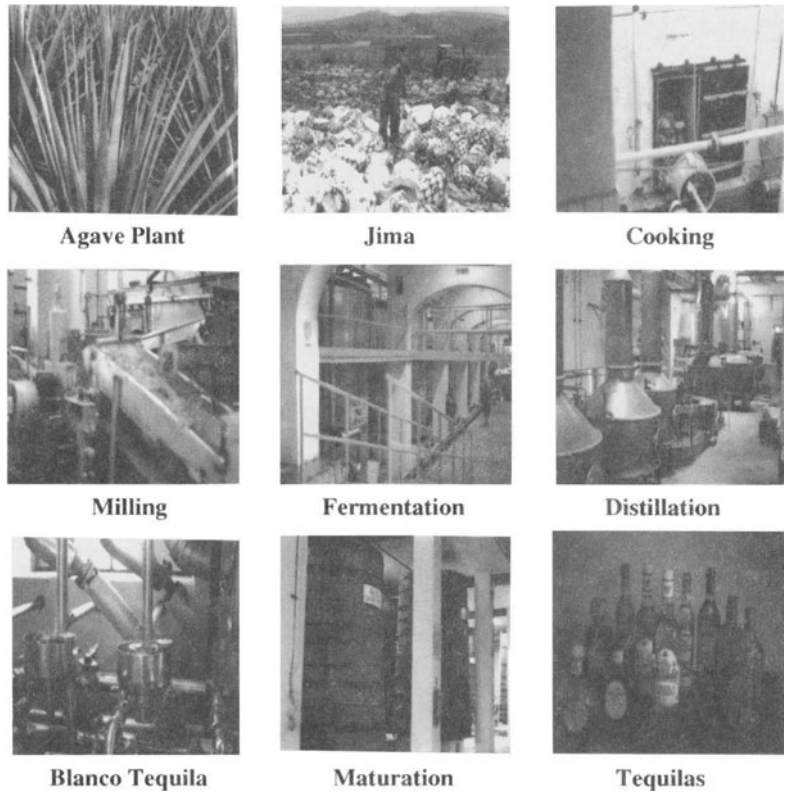


Figure 15–10 Tequila production scheme.

pyran-4-one (DDMP). Most of these compounds are generated through the Maillard reaction (López and Mancilla-Margalli, 2000). Other non-Maillard compounds found in the exudate were fatty acids (C_2–C_{18}), aldehydes, alcohols, some terpenes and vanillin. The kinetic behavior of some relevant Maillard compounds generated during the cooking process showed a dramatic increase between 16 and 20 hours with a subsequent decrease, including 5-HMF, which is the largest Maillard compound throughout all the collected samples (López and Mancilla-Margalli, 2000).

Fermentation

The fermentable tanks must be of stainless steel to resist the acidity of the agave juice which pH can be as low as 4.0. Generally, the capacity of the tanks is between 12,000 to 50,000 L. For a 100 % Tequila the wort is adjusted to a 4–5 °Bx and for mixed type to a 10–12 °Bx. Once the wort is formulated with all the required nutrients (mineral salts and nitrogen compounds, to mention some), the temperature is set between 30 and 42 °C and maintained in semi-anaerobic conditions (Alvarez, 1996). In general, the wort is inoculated with specific strain of *Saccharomyces cerevisiae* to reach a concentration of 10^7 and 10^8 cell/mL. The strain may vary from company to company, however, to reduce variability on the tequila characteristics many distilleries use yeast isolated from the natural fermentation of the agave juice. Some other companies prefer a natural fermentation, this means that they do not add any strains, however, due to the large variability of micro-organisms in the agave juice, the overall flavor of the tequila can be highly affected.

Fermentation time usually depends on the type of strain used and can oscillates between 1 and 3 days, but during natural fermentation, it can even last 10 days. However, other parameters such alcohol concentration are also taken into account before stopping the fermentation process. For instant, the final alcohol concentration for tequila during this step for a 100 % agave type must reach a 6 % and at least 4.5 % for a mixed type.

Distillation

Distilling systems used in the Tequila companies include pots still and rectification columns. The pot still is the most common systems used, consisting of two pots stills in tandem made out of copper. As in many other distilling beverages, copper eliminates some undesired flavors in the product.

The first pot still is known as "ordinario" and is mainly done to remove solid particles, yeast, proteins and mineral salts. Here, steam is used as heat to distillate off the dead wort until an alcohol concentration of about 25 to 30 % is reached. The heads contain principally volatiles such as acetaldehyde, methanol, isopropanol and ethyl acetate. Tails, on the other hand, contain amyl alcohol, iso-amyl alcohol, some esters, furfural and acetic acid which impart unpleasant characteristics to tequila.

The second pot still is the distillation of the "ordinario" and the main objective is to increase the alcohol concentration up to 55 %. The tequila obtained at this point is known as "Tequila Ordinario", this product can be sold as such. However, if it is bottled, it must be diluted with demineralized water to lower the alcohol to a 30 to 42 °GL, this tequila is called "Tequila Blanco" (white Tequila) (Alvarez, 1996).

Maturation

White Tequila can be matured in two different ways to produce what is known as "Tequila Reposado" (rested Tequila) and "Tequila Añejo" (aged Tequila).

The NOM establishes that Rested Tequila must be matured in 200 L white oak casks or in larger wooden tanks called "pipones" from three to six months. On the other hand, aged Tequila must be kept in 200 L white oak casks only, for at least a year (Cedeño, 1995).

Depending on barrels type and maturation time Tequilas will have very distinctive flavor characteristics. As is the case with other alcoholic beverages.

Flavor Chemistry

In general, very few papers have been published on different aspects of the tequila process and tequila flavor characteristics. The oldest information on tequila composition dates from 1969 by Manjarrez and Llama. These authors published the main volatiles in 15 tequilas and 8 mezcals (another Mexican beverage). Incitti *et al.*, in 1980 reported 25 minor volatiles in some tequilas using a gas chromatography with a packed column.

Three years later, Bluhm (1983) also reported some differences observed on aged tequilas. More than a decade later, Benn and Peppard (1996) performed a very representative study on the characterization of tequila flavor components by instrumental and sensory analysis. These authors reported more than 175 volatiles in three different types of tequila. Among these compounds esters (47), alcohols (22), acetals (24), terpenes (25) and furans (14) were the most abundant, however, many other groups of compounds such as acids (11), aldehydes (8), ketones (12), phenols (8) and sulphur (3) compounds were also present. It is very likely that most of the esters identified in this study are the result of yeast metabolism or they are formed during the ageing process by the reaction of fatty acids with the compound in excess, ethanol. Most alcohols are also generated during fermentation. On the other hand, the authors state that most terpenoids might come from the agave plant. Many other compounds must be formed during the cooking process (see Harvesting, cooking and mashing). Quantitatively, the most abundant volatiles in this study were 2- and 3-methylbutanol (491 ppm) followed by 1-propanol (232 ppm), 2-methylpropanol (228 ppm) and ethyl acetate (176 ppm). In this same paper, 60 compounds were identified as odorants and half of them were characterized completely by AEDA studies. Table 15–7 lists the most potent volatiles in this study.

The authors tried to reconstruct the tequila flavor profile mixing all the most potent odorants, however, they were not successful on reproducing the tequila aroma.

In another tequila aroma study, López (1999) reported the presence of 163, 175 and 198 volatiles for Blanco, Reposado and Añejo, respectively. Most of the identified compounds were alcohols, esters, acids and furans, along with some

Table 15–7 Aroma extract dilution analysis of some tequilas

KI	*DF*	*Descriptor*	*Compound*
1,179	12,800	Fruity, woody winey	β-damascenone
>1,800[a]	12,800	Sweet, creamy	Vanillin
249	6,400	Sweet, cocoa, chocolate	Isovaleraldehyde
581	6,400	Sweet, fruity, fusel	Isoamyl alcohol
1,280	6,400	Floral	2-Phenylethyl alcohol
1,225	3,200	Smoky, phenolic	Not identified
1,629	3,200	Fatty acid, dry, woody	Decanoic acid + ethyl hexadec-9-enoate
1,568	1,600	Warm, spicy, curry	Thymol + unknown
>1,800	1,600	Woody	Not identified

KI, Kovats indices; DF, dilution factor.
[a]Larger than the series of ethyl esters used to determine the KI. DF, Dilution Factor.
From Benn & Peppard (1996).

Table 15–8 Impact aroma compounds in tequilas

KI	*Descriptor*	*Compound*
1,092	Tepache	Unknown
1,101	Tequila	Unknown
1,223	Sweet	2/3-Methylbutanol
1,275	Floral	Phenylethyl acetate
1,567	Sweet, floral	Linalool
1,887	Woody, fruit	Phenylethyl alcohol
2,248	Butter	Decanoic acid
2,277	Warm-phenolic	Unknown
2,538	Tequila	Unknown
2,552	Very sweet	Vanillin

KI, Kovats indices in a HP-FFAP column.
From López (1999).

terpenes and nitrogen compounds. The author also reported the impact compounds in these three classes of tequila. However, four of the impact volatiles were not chemically characterized.

López and Dufour (2001) presented the most potent odorants in Blanco, Reposado and Añejo Tequilas by Charm analysis (Table 15–8). Figure 15–11 shows a typical aromagram/chromatogram profiles of a Tequila sample.

It is important to mention than the main differences among the three types of tequilas were quantitative and not qualitative. In general, more highly volatiles compounds were present in Reposado and Añejo tequila types that in the non aged tequila. Nevertheless, many odorants are common to all samples.

In spite of the large similarity of odorants in all tequilas, it is clear that the most potent odorants in each tequila varied not only in number but also in intensity. For example, the three more active odors were present in the last dilution serial of Blanco tequila. On the other hand, Reposado tequila presented six potent odorants responsible of its flavor and Añejo tequila only displayed two very relevant odorants. Therefore, it can be said that the Reposado tequila has a more complex overall aroma than the other two types of beverages, independently of the large difference in resting times; Reposado usually takes two months and Añejo at least six months.

It is relevant to mention that the three most potent odorants in Blanco tequila are three of the six important volatiles in the Reposado type. But, only one of the two most potent odors in Añejo tequila was also relevant in the Reposado.

Figure 15–12 presents the Charm chromatograms of the three tequilas. It is obvious from this results that Reposado and Añejo tequilas have a more complex aroma profile than Blanco tequila. This must certainly be related with the ageing processes of each tequila (López and Dufour, 2001).

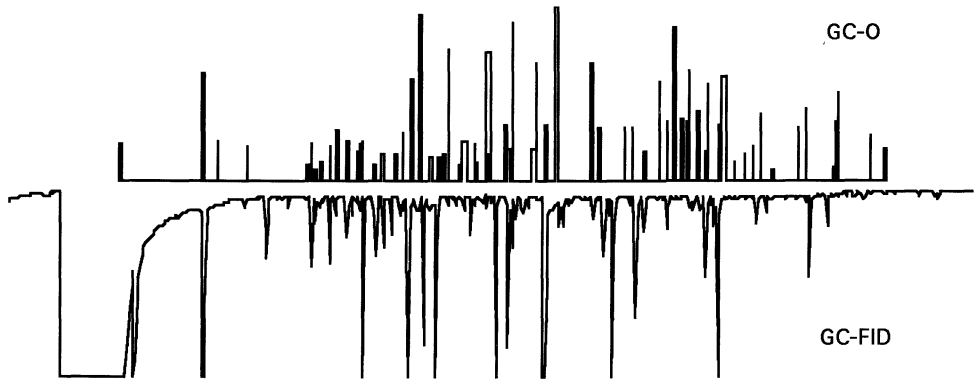


Figure 15–11 Analysis of Tequila Blanco extract by GC-O (aromagram) and GC-FID (chromatogram).

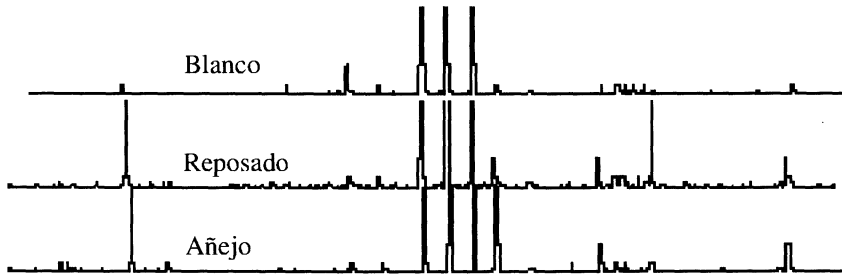


Figure 15–12 Charm response chromatograms of Tequila Blanco, Reposado, and Añejo.

Finally, Table 15–9 lists the most potent odorants found in the three types of tequila by Charm analysis. It can be seen that most of the impact compounds are present in all tequila types, however, Añejo tequila displayed the highest Charm values, therefore, Añejo tequila have a more complex overall aroma.

Table 15–9 Most potent odorants in all tequilas

			Charm values		
KI	*Compound*	*Descriptor*	*Blanco*	*Reposado*	*Añejo*
1,030	Unknown	Solvent	748	845	2,842
1,200	Butanol, 3-methyl	Alcohol, vinous	2,407	2,065	6,515
1,659	Decanoic acid EE	Fatty	267	400	357
1,809	Phenylethyl acetate	Tepache, floral	1,564	2,415	3,035
1,862	Unknown	Medicinal	880	1,501	2,221
1,906	Phenlylethyl alcohol	Sweet, floral	6,083	4,560	7,771
1,953	Unknown	Plastic		1,644	16,956
2,166	Eugenol	Medicinal, sweet	941	1,498	2,403
2,201	Terpenoid	Chicken	1,259	2,241	4,733
2,266	Decanoic acid	Fatty		411	2,102
2,555	Vanillin	Vanilla, sweet	1,959	3,641	5,510

KI, Kovats indices.
Lopez & Dufour (1999).

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16

Filtration and Stabilization of Beers

G. J. Freeman and M. T. McKechnie

BACKGROUND TO BEER STABILITY

There is a distinct trend in the brewing industry for centralization of brewing capacity into fewer, larger breweries. Production costs are thereby minimized according to the principles of economy of scale. However, these trends necessitate extended distribution networks for products. The subsequent increase in the interval between production and consumption has put pressure on brewing companies to provide beers with longer and longer shelf-lives. This chapter will outline the processing operations used to render beer stable for subsequent packaging. The processes from fermenter to bright beer tank will be covered. The main part of this document will refer to bulk beer production but specific mention of cask ale production will be made. Other beverages are not specifically discussed but where there is commonality in processing in cider making this will be highlighted.

The stability of a beverage can be divided into three aspects: microbiological, colloidal and flavor stability.

Microbiological and colloidal stability may be achieved by the dual application of good manufacturing practice and stabilizing processes prepackaging. The use of stainless steel plant throughout and C.I.P. (cleaning in-place) systems which are fully automated have enormous benefits for product consistency. In the case of beer, most haze precursors are derived from the malted barley. There are opportunities throughout the process to remove particulates prior to the final clarification stage(s) and these opportunities should be taken. Both product quality and stability necessitate careful handling of yeast, such that no excessive conditions (pressure, temperature, shear regimes *etc.*) are encountered and yeast lysing or release of unfavorable (taste, foam negative) components are avoided.

The most common stabilizing approach in modern beer production is the sequence cold storage-bulk filtration-pasteurization. Many of the suspended solids settle out during the cold "rest" and these "tank bottoms" are run off and handled separately. Bulk filtration of the supernatant is most frequently effected by kieselguhr filtration. Pasteurization may be performed online via a flash pasteurizer or in small-pack by tunnel pasteurization. Alternatively, microbiological stability may be obtained by membrane filtration. Effective sterility may also be achieved by a

very fine depth filtration operation such as sheet filtration. Such a polishing filtration operation is often included after bulk filtration in any event for the attainment of excellent product clarity and colloidal stability. Solids removal may be aided by centrifuges which lower the solids load onto kieselguhr filters.

For long shelf-life (more than three months) it is advisable to use further stabilization agents which reduce the levels of potential haze-formers in the beer.

Through application of the above techniques, microbiological and colloidal stability are ensured such that they rarely become the parameters controlling shelf-life. It is the deterioration in flavor which determines the lifetime of a beer. Beer develops stale flavors such as "cardboard" and "blackcurrant" while some beneficial flavor notes may decline. These effects are caused by complex chemical reactions in the beverage, many of which involve oxygen.

THE IMPORTANCE OF OXYGEN

It is increasingly recognized that exclusion of oxygen throughout the brewing process is necessary if prolonged flavor life is to be achieved. Traditional practices of wort production from malt (wort is the sugar and nutrient solution which is fermented to make beer) has taken no account of pick-up of oxygen. However, absorption of oxygen into hot wort during its preparation can cause deterioration of flavor stability of the end product (Clarkson *et al*, 1992). Only in fermentation and in the malting of barley is oxygen deliberately employed in the process.

After fermentation oxygen must be excluded from the beer at all times. Oxygen ingress is prevented through the purging of the beer by the carbon dioxide produced. Conditioning tanks should always have positive pressure (even if carbon dioxide is added in-line) and there is the option of employing oxygen scavengers.

Due to the low pH of beer (typically 4.0), the alcohol content and also the presence of hop compounds (Simpson, 1993) few species of micro-organism can grow in beer. None of them are pathogenic. Micro-organisms that contaminate yeast such as "wild" yeasts and the gram positive bacterium *Pediococcus damnosus*, can be minimized by use of a freshly propagated batch of yeast every ten fermentations or so, and by the application of acid washing of the yeast (Simpson and Hammond, 1990). Another group of gram-positive bacteria that can spoil beer are lactic acid bacteria such as *Lactobacillus brevis*. They normally require sources of carbohydrate and amino acid but do not require oxygen. In the presence of oxygen the product is extremely susceptible to spoilage by acetic acid bacteria such as *Acetobacter* and *Acetomonas*. Minimization of oxygen post-fermentation precludes the growth of acetic acid bacteria. They may still be a threat to the stability of traditional cask ales and in beer lines at dispense. Other contaminating organisms, such as *Zymomonas mobilis*, *Pectinatus* or *Bacillus* are encountered more rarely.

Non-biological haze formation in beer is generally a consequence of protein-polyphenol interactions, although occasionally hazes are found which comprise other substances such as starch, calcium oxalate or b-glucans. Oxygen stimulates haze formation by promoting the interactions of proteins and polyphenols.

Oxygen has been shown to have a crucial role in flavor deterioration. Unsaturated fatty acids in wort are oxidized, forming precursors of carbonyl compounds such as *trans*-2-nonenal which give stale flavors in beer. There is some debate as to whether this oxidation is catalyzed by enzymes, such as lipoxygenase, or is non-enzymic and stimulated by transition metals such as copper or iron. Minimization of dissolved oxygen in package is crucial. The effects of oxygen in brewing have been reviewed in much greater detail elsewhere (Bamforth *et al*, 1993).

In a modern brewery oxygen levels below 0.2 mg/l are readily attainable in the packaged product. Alternatively antioxidants such as ascorbic acid or sulphur dioxide are sometimes employed (Marchbanks, 1986).

COLD CONDITIONING

Upon completion of fermentation, beer undergoes flavor maturation followed by stabilization. These three stages of the process are not always completely distinct. Flavor maturation is already under way by the end of fermentation and beer maturation and colloidal stabilization by cold rest occur simultaneously in some systems. For instance, traditional "lagering" may entail storage at 4–6 °C for 3-6 weeks. Alternatively, the "ageing" process may occur at 2 °C for several days. In the UK most lagers have a flavor maturation stage known as "warm conditioning" at 10–16 °C for a few days, followed by the stabilizing "cold conditioning" at −1 °C.

The majority of beers are cold conditioned in cylindroconical tanks (Figure 16–1) and the temperature is lowered and controlled via jackets on the vessel walls. Cooling is achieved by secondary coolants such as ethylene glycol. There is normally a jacket on the vessel cone and one or two jackets higher on the walls. The first part of the cooling is performed largely by the upper jackets and the temperature is monitored by probes towards the base of the vessel since colder beer tends to sink. However, as with water, beer reaches a peak density at *ca.* 4 °C and so at this point the cooling system reverses, cooling is concentrated lower down the vessel and is monitored by probes higher up the vessel to ensure freezing does not occur.

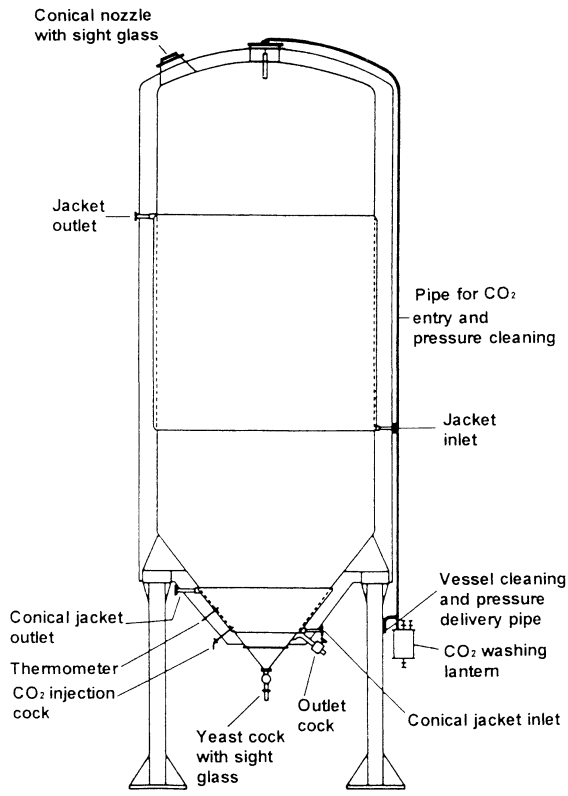


Figure 16–1 Cylindroconical brewery vessel used for cold storage.

Allowing for the production schedules within a brewery, a typical cold conditioning operation may be for one week. However this is the key buffer stock stage for the brewer, with beer at its most durable at this period of the process.

The main objective of cold conditioning is to prolong the colloidal stability of the product in package. The volumetric bulk of the suspended solids (mostly yeast) settle into the cone to be removed and processed separately. The most significant stabilizing effect is the formation of "chill haze". Polyphenolic and proteinaceous components cross-link through hydrogen bonding. The resultant particles are known as chill haze since they would immediately re-dissolve if the beer temperature was raised. However, if not removed from the product they eventually form the more thermostable "permanent haze" by replacement of the hydrogen bonds with much stronger covalent bonds. Thus these particles are deliberately formed by cold conditioning, to be removed by fine filtration (they are typically less than 3 microns in size).

CONVENTIONAL POWDER FILTRATION

The bulk filtration duty in a brewery is a demanding unit operation. It is essential for product clarity, and also for colloidal stability. It should significantly lower the quantity of contaminant micro-organisms presented to the pasteurizer, since heat should be used sparingly if flavor impairment is to be avoided. If sterile filtration is employed the bulk filtration stage must still give a high degree of clarity since the majority of sterile filtration systems have very limited dirt-holding capacities.

These difficulties are further enhanced by the nature of unfiltered ("rough" or "green") beer. The low temperature (0 °C) and presence of dissolved solids and alcohol means that viscosity is quite high (at least 2 mPa.s). Of even more significance is the nature of the suspended solids. These may be present in very high levels, perhaps up to 0.2 % by volume or even higher over short periods during tank run-off. The level of solids may be reduced by the use of finings, shallow conditioning tanks or more flocculent yeast strains. Practically all of the suspended beer solids are compressible, which causes them to form filter cakes impermeable to beer flow. Accordingly, filtration directly onto a cloth is rendered impractical. Finally, beer presents more of a filtration problem than do many other beverages because of its "chill haze" particles, which are very compressible indeed. They often prematurely "blind" the inner layers of filtration media. The volumetric proportion of these solids in unfiltered beer is seldom greater than 0.015 %. A typical solids distribution of an unfiltered beer (as analyzed by Coulter Counter) (Morris, 1984) is shown in Figure 16–2. Filtration may also be impaired by colloidal substances such as β-glucan gels (Narziss *et al*,1990).

The problem of impermeable filter cakes is currently solved in breweries by the use of filter aids. These substances, used as slurried powders, form incompressible and highly porous filter beds, thus allowing the relatively free flow of beer. The most common filter aid used in breweries is kieselguhr or diatomaceous earth (Figure 16–3). These materials comprise of fossils or skeletons of microscopic salt or freshwater life known as diatoms. When they die they sink and form deposits which are mined, processed and size-classified to give kieselguhr of various grades. The disadvantages of kieselguhr are that it is a health hazard (by dust inhalation) in its dry form as delivered to the brewery and that it is non-biodegradable and thus expensive to dispose of in landfill sites.

Alternative filter aids (and alternative technologies) are therefore sometimes used. Perlites consist of thermally-expanded volcanic glass, crushed to form microscopic flat particles (Figure 16–4). Perlites are less efficient filter aids than are kieselguhrs, although they have higher dirt-holding capacities. They are perceived as being safer. Other substances which may be used on occasions include cellulose (as coarse grades) (Speckner, 1985) and various types of silica gel, the latter having the benefit of selectively adsorbing haze-forming proteins (McMurrough *et al*, 1993).

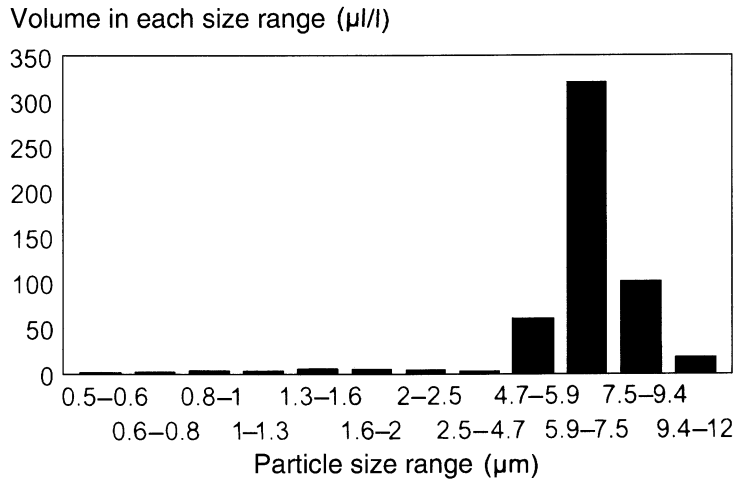


Figure 16–2 Typical solids size distribution of an unfiltered beer (Coulter Counter analysis) (Morris, 1984).

With regard to the actual filter, options may be divided into plate and frame type and vessel type.

Plate and frame filter presses (Figure 16–5) are the most established of these technologies. The beer feed is into the base of the frames in which the cake build-up occurs. The cake is deposited onto filter cloths which are held in place by the plates. These differ from the frames in that they have rigid mesh on each side for retention of the cloth and cake. The filtered ("bright") beer passes out through channels in the top of each plate.

Vessel filters are of two types: candle filters and leaf filters. Candle filters (Figure 16–6) comprise cylindrical filtration surfaces and the beer is filtered from outside the candles to a channel inside and then out to bright beer tank. The filtration surface may consist of a quantity of metal

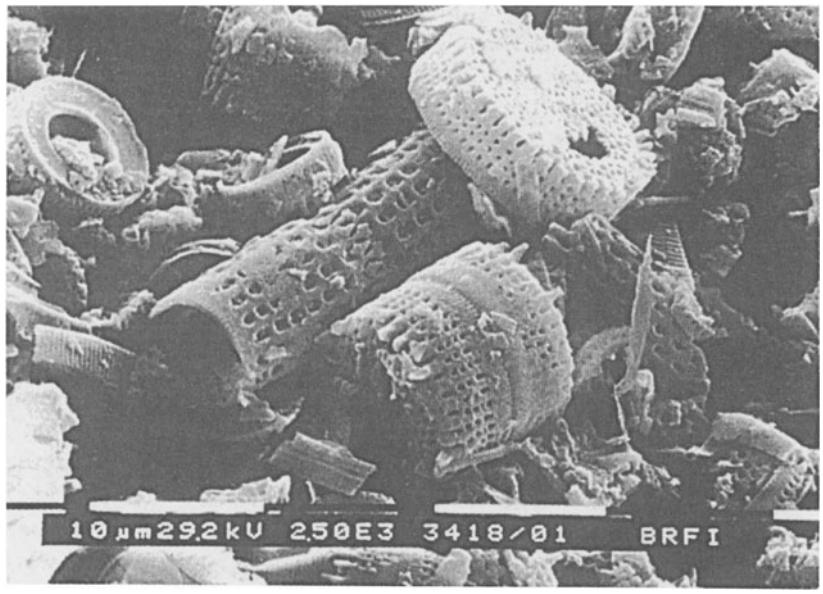


Figure 16–3 Diatomaceous earth, magnification approximately 1,500 (courtesy of Eagle Picher Industries, Inc.).

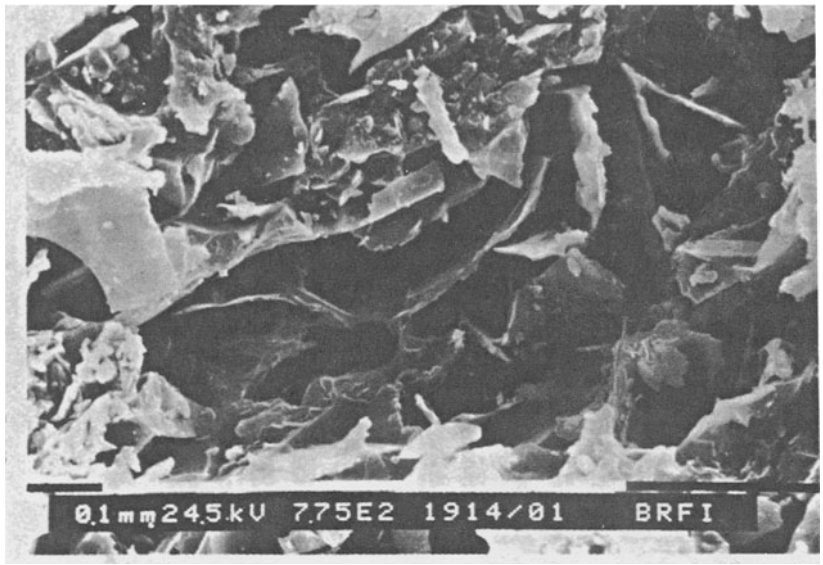


Figure 16–4 Electron micrograph of a typical bed of perlite, magnification approximately 1,000.

discs which are "threaded" together and "ridged" so that there are small gaps (ca. 100 microns) between each disc in the candle. Alternatively, the surface may be a helically wound metallic structure (Woodruff *et al*, 1981).

Leaf filters comprise stacked mesh plates (Figure 16–7), and the filtration is onto the outer surface of the mesh and the bright beer is channelled from inside the "leaf" to the bright beer tank. This type of system is found in vertical leaf and horizontal leaf forms and some modern designs incorporate flow distribution systems ensuring even distribution of the cake onto the leaves (Oechsle, 1991).

Comparisons of the performance of the various filters are a matter of some dispute. The rugged construction and flat geometry of the filter surfaces in plate and frame filters are said to

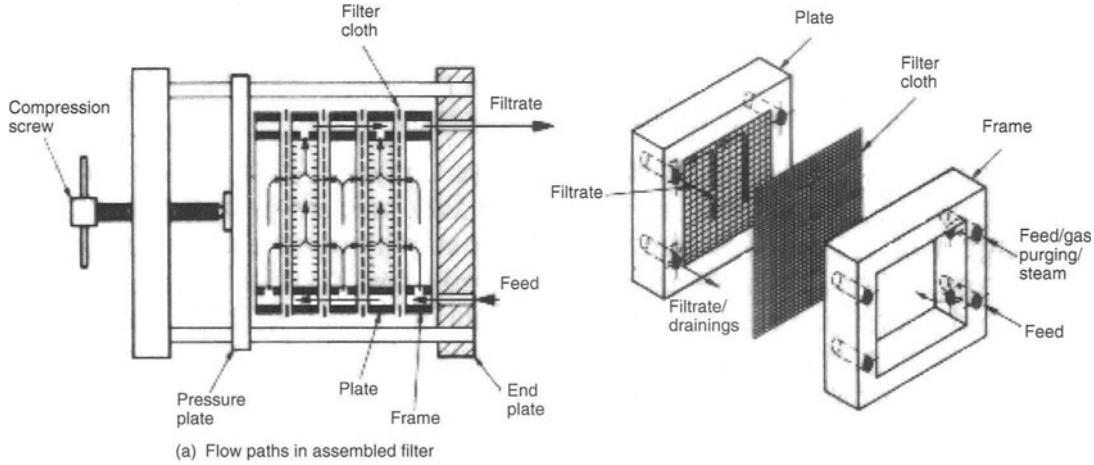


Figure 16–5 Diagrammatical representation of filtration by a plate and frame filter press (Murray, 1993).

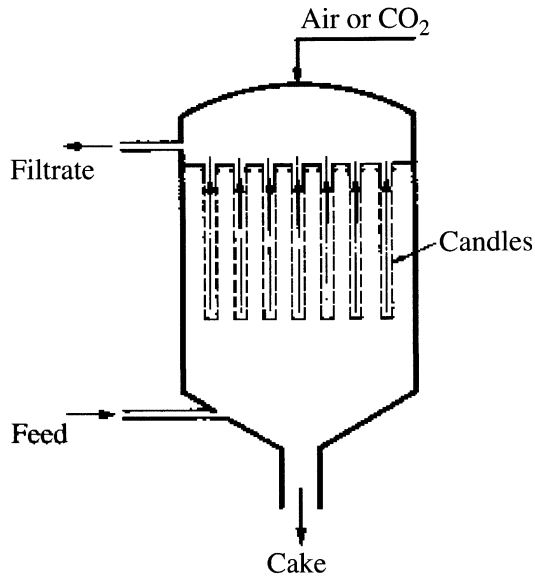


Figure 16–6 Candle filtration (Murray, 1993).

give the clearest filtrates of all. However, there is the potential for the filtration surfaces in leaf filters to flex slightly due to pressure drop across the cake. If this occurs a deterioration in filtrate quality would be observed. Vessel filters in general might not be expected to give as high quality filtrate as plate and frames due to the higher flowrate loading per unit surface area. The "no moving parts" construction of candle filters causes maintenance requirements to be minimal. The main disadvantage of plate and frame filters is that they are not readily automated. At the end of filtration the press must be opened, the cloths scraped and hosed down manually and the press re-assembled. Such an operation is time consuming (a turn-around time of up to four hours depending on the number of operators) and labor-intensive. Leaf filters are the most readily automated, since after a gas purge the dry cake may be spun off the leaves by turning the central axis. Candle filters may be backflushed after "chasing" the beer out with liquor.

Long filter runs in the brewery are achieved by dosage of aqueous filter aid slurry into the unfiltered beer as it flows into the filter. Thus the beer is being filtered by a filter surface that is constantly being regenerated.

Before processing occurs a precoat of filter aid is deposited onto the filtration surface. This is achieved by recycling of a water/filter aid slurry around the filter, normally at 50 % higher flowrate than the rating of the filter. The higher flowrate ensures even deposition of the precoat. Included in the recycle loop is a precoat tank in which the required dosage of precoat filter aid is slurried. After several minutes the precoat will be deposited completely onto the filtration surface and the recycling water is clean. The precoat is necessary to ensure efficient filtration of the early part of the beer run and, even more importantly, to guarantee the integrity of the filter throughout the run. Common loadings of precoats are 500–1000 g/m^2 of filter surface (roughly equivalent to a 1–2 mm layer thickness). Depending on the nature of the filter surface, more than one precoat layer may be used. For instance, the metallic structures commonly used in candle filters or leaf filters will require an

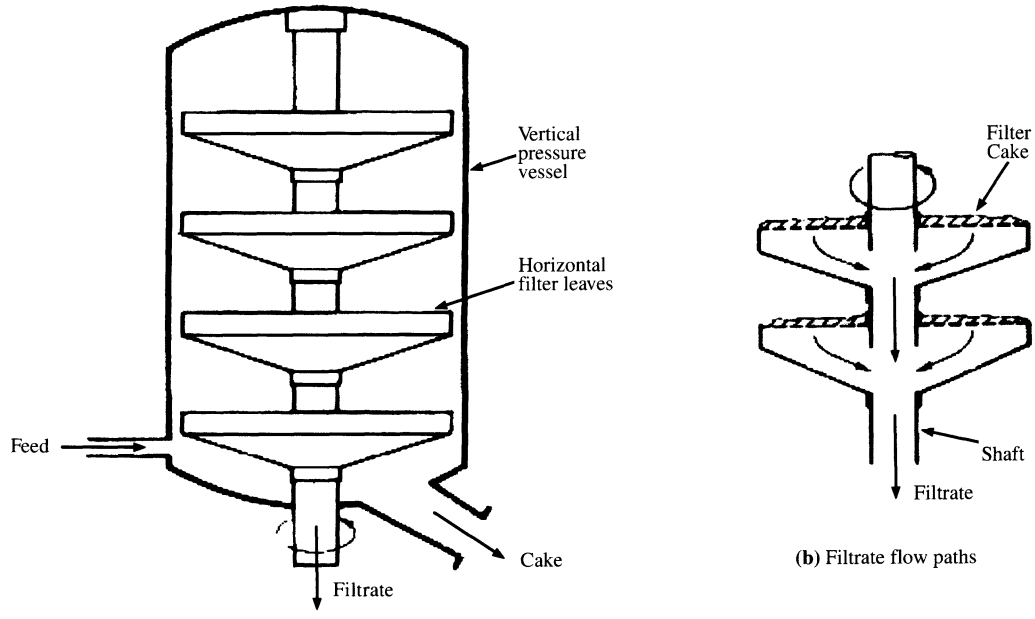


Figure 16–7 Diagrammatical representation of a horizontal leaf filter during cake discharge (Murray, 1993).

initial coarse precoat (perhaps of perlite or flux-calcined kieselguhr) (Candy, 1991) to retain the relatively fine powders used for the filtration.

The flux-calcination process employed for production of coarse grades of kieselguhr agglomerates diatoms, thus increasing particle size. The production of the relatively fine grades needed for bodyfeed dosage most commonly incorporates a less severe calcination stage which also results in minimization of contamination to the product. Kieselguhrs are size classified by the suppliers to give a range of specifications: bodyfeed grades have permeabilities between 0.02 and 0.5 Darcies.

After precoating, the filter is smoothly put into "forward flow" mode. At all times it is essential to avoid "pressure shocks" which can damage the integrity of the filter cake. For this reason it is good practice to have a buffer tank installed in the line just upstream of the main delivery pump to the filter. This will eliminate any flow inconsistencies in what may be a long line from the conditioning tank. The filter is normally run at constant flowrate, and the run ends when the inlet pressure limit is reached. The flow rating of the filter depends upon its filtration area. Plate and frame filters are rated at approximately 0.3 $m^3/h/m^2$ and vessel filters at up to twice that figure.

Slurried filter aid is dosed directly into the beer main ahead of the filter. The average mass of filter aid (as dry powder) used per unit volume of beer in breweries (including precoats) is approximately 1.15 kg/m^3. Reduction of this figure requires in-line analysis of suspended solids and automated dosage control of well-characterized filter aids. Such a system is effective in production (Freeman, 1999).

The health hazard associated with filter aids causes their handling in breweries to be somewhat arduous. Emptying of the sacks of filter aid for slurry preparation occurs in a dedicated filter aid handling area incorporating powerful extraction equipment by personnel equipped with dust masks and protective clothing. The powder system incorporates conveyors for the dry filter aid feeding large bodyfeed mix tanks, wherein a slurry of perhaps 10–20 % by weight of filter aid

in clean water is prepared. These tanks probably feed smaller "dose tanks" closer to the beer main. Both tanks must be continually agitated otherwise the filter aid rapidly settles. It is good practice in the "dose tank" to de-aerate the slurry by gas purge and to maintain an oxygen-free atmosphere to prevent oxygen ingress into the beer. The dosing is performed by small positive displacement pumps suitable for thick slurries and pumping against variable pressure. The pumps and filter aid lines must be purged with water at the end of filtration to avoid blocking the lines.

Spent filter cake is deposited into a collecting trough, from when it is routed by pumping (thin slurry) or screw conveyor (thick slurry) to disposal. Disposal is to landfill sites, the charges for which are increasingly substantial. In some countries disposal has even been banned and so recycling of spent kieselguhr has been considered. The problem with recycle is that often kieselguhr agitation in slurry tanks damages the skeletal particles, thereby reducing their effectiveness. Therefore, it is not advantageous to filter with 100 % recycled kieselguhr, although recycling up to 50 % may be viable. Regeneration relies on destruction of beer solid residues in the spent cake. This can be achieved by chemical treatment using caustic solutions (Russ, 1993), by heat treatment (Fischer, 1992) or possibly with hydrocyclones (Rickwood *et al*, 1996).

In a modern brewery the "haze" (clarity) of the filtered beer is normally monitored by in-line nephelometry (Wackerbauer *et al*, 1992). Causes of poor filtrate clarity might include use of filter aids that are too coarse, a higher proportion of smaller sized solids in the beer or leakage of "fines" from the filter aid through the filter. There is also the possibility of sudden "breakthrough" of part of the filter cake. To safeguard product quality against this, a "trap" or "guard" filter may be placed in the line downstream of the main filter. Such equipment normally consists of a 10–20 micron nominally rated cartridge filter.

An interesting variation on the theme of poor filtrate clarities are "invisible hazes" or "pseudo-hazes". These consist of particles considerably less than 0.5 microns (Jackson and Bamforth, 1983). As such they are not removed by the beer filter, and also cannot normally be perceived by the naked eye. They do however deflect plane polarized light and therefore cause high readings from nephelometers (especially those that measure scatter to 90° from transmitted light) (Buckee *et al*, 1986) without being a "haze" detectable to the consumer.

In the future, crossflow membrane microfiltration (CFMF) may replace diatomaceous earth filtration (Noordman *et al*, 1999). In CFMF beer is pumped at high velocity (1–6 ms^{-1}) through a narrow channel of 1–5 mm dimension (so-called crossflow or tangential flow) above the surface of a porous microfiltration membrane which is a thin polymer or ceramic film with well defined pores typically of 0.1–1.0 μm. These channels can be cylindrical, parallel plates or even a complex spiral wound "Swiss roll" configuration. The differential pressure in the crossflow channel is controlled such that fluid is forced through the membrane pores (Figure 16–8). The filter is a surface filter (micro-sieve) and is very prone to blinding. The function of the crossflow is to minimize the build up of separated solids. However solids do build up, leading to membrane fouling. This build up of debris can become so severe that the filtered beer can be deprived of essential components such as color, head retention proteins, bitterness and gravity (Reed *et al*, 1989). If the membrane is correctly selected than it is possible to generate a sterile product.

STABILIZATION WITH PROCESSING AIDS

This section will cover the practice of using stabilizing aids in the cold conditioning and filtration stages of bulk beer stabilization. We will not deal with finings which will be discussed in the section on production of cask ales, although these can also be added into conditioning vessels during bulk beer production.

Processing aids are defined as "substances or materials—not including apparatus or utensils—

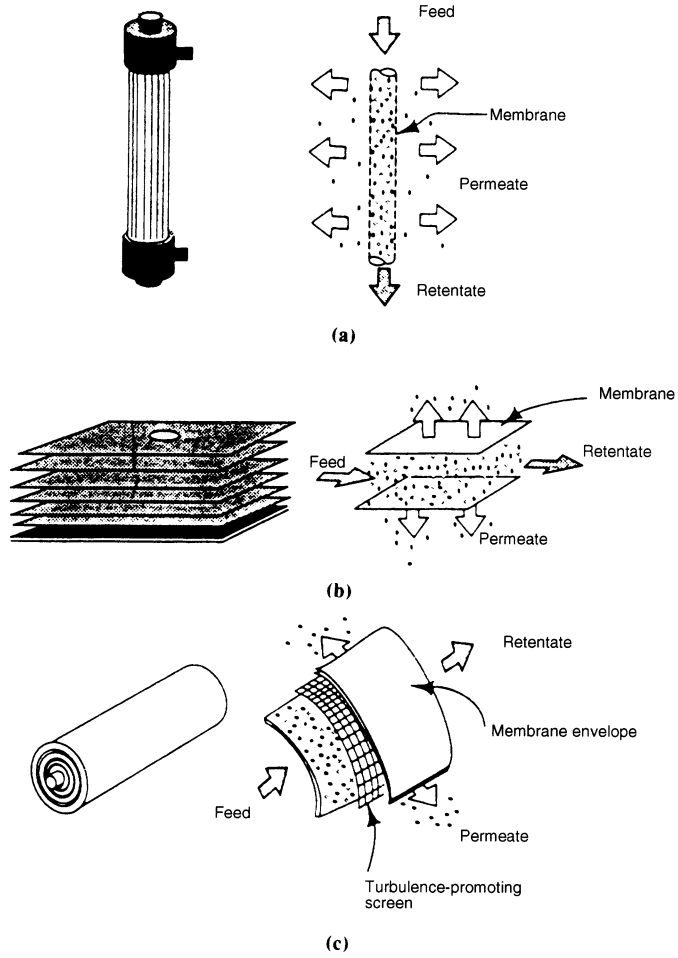


Figure 16–8 Crossflow membrane module configurations (Ryder *et al*, 1988).

which are used to fulfil certain technological purposes during treatment or processing, and which may result in the non-intentional presence of trace residues in the final product" (UK Ministry of Agriculture, Fisheries and Food, 1979). Additives, by contrast, remain in the product.

Excellent summaries of additives and processing aids most commonly used in brewing operations were given by Marchbanks (1986, 1989). A summary of stabilizers has been adapted in Table 16–1. The use of ascorbic acid and sulphur dioxide is covered briefly in the sections on oxygen and cask ales. Both of these additives are heavily used in cider making to prevent oxidation of fruit pulp and of the finished product.

Tannic Acid

Tannic acid is used to accelerate haze formation during processing by enhancing precipitation of complex nitrogenous material. It also has a secondary effect as an oxidizing agent. Tannic acid (Figure 16–9) is natural and is usually extracted from gall nuts. Molecular weight is typically between 500 and 2500 and tannic acids for use in brewing consist of both monomeric and

Table 16–1 Stabilization process aids and their properties

Material	*Material type*	*Typical rate of usage (g/hl)*	*Effect upon*[a]			
			Prot	*Phl*	*Oxi*	*Head*
Papain	enz	1–2	+			–
Tannic acid	ads	3–10	+	+	–	–
Isinglass finings		2–4	+			+
Auxiliary finings	ads	0.5–1	+			
Bentonite	ads	50–75	+			–
Silica gel	ads	70–200	+			
Nylon	ads	25–50		+		–
PVPP	ads	5–25		+		
Active carbon	ads	30–80	+	+		
SO_2	add	1.0–2.5			+	
Ascorbic acid	add	2–5			+	
Glucose oxidase	enz				+	
Propylene glycol alginate	add	2–5				+

add, additive; ads, adsorbent; enz, enzyme.

[a]These columns indicate the positive (+) and negative (–) effects, in terms of product stability, dispensing, or organoleptic properties, on proteins (Prot), polyphenols (Phl), oxidation (Oxi), and head retention (Head).

Adapted from Marchbanks (1986).

dimeric acid species. Care should be taken to avoid excessive use as phenolic oxidation products can be formed from uncomplexed tannic acid. Acidic proteins in the range of *pI* 3.5–6.5 are specifically removed. Tannic acid may be added into cold conditioning vessels but "fluffy" tank bottoms can arise which take up excessive volumes of beer. A new generation of gallotannins has been prepared for addition just ahead of filtration. A residence time of at least 15 minutes is achieved using a buffer tank. The duty on the filters is reduced by centrifugation (Mussche and de Pauw, 1999).

Silicas

A wide range of amorphous silicas is available but basically function is by one of two mechanisms:

1. Selective adsorption of haze forming proteins by interaction with surface silanol (SiOH) groups. The mechanism involves hydrogen bonding between protein carbonyl groups and silanol hydroxyl groups.
2. Permeation of these captured proteins into the pores, which is a selective process dependent upon pore size and structure.

This latter mechanism has been postulated as the reason that the haze-forming proteins (molecular weights from 1,000–40,000) are removed whereas the higher molecular weight foam positive proteins are not. New work however, has suggested that the selectivity is according to the chemistry of the proteins and that those which incorporate the imino acid proline are especially inclined to adsorption (Siebert, 1997).

Pore sizes are typically of the order of 4–8 nm, while surface areas are of 300–1000 m^2/g. The particle size distribution of the silicas should not include a large proportion of fine material (< 5 microns), otherwise filtration problems will occur (Hough and Lovell, 1979).

For beer stabilization duties silicas are manufactured by one of two routes, based upon the reaction of sodium silicate with mineral acid. The gel route uses precipitation under carefully controlled acidic conditions with subsequent washing of the gel to remove the by-products

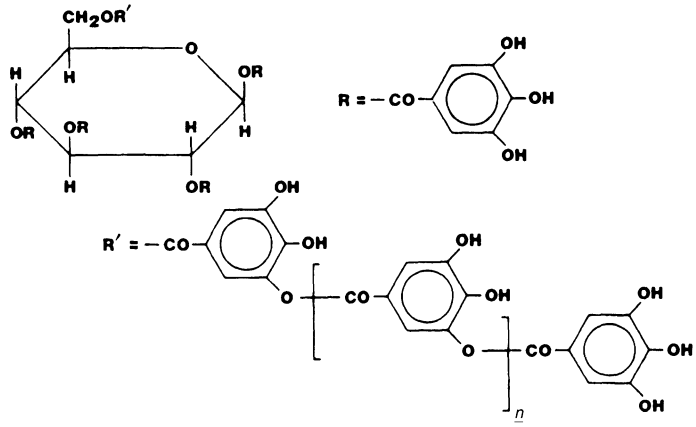


Figure 16–9 Tannic acid.

(sodium silicate and sodium sulphate). Ensuing milling and classification will give a hydrogel, whereas subsequent drying and milling/classification gives a xerogel. The precipitation route involves destabilization of the polysilicic acid anions by partial neutralization at high pH followed by washing, drying and milling/classification.

One other generic type of silica is used, the aerogel which is formed by replacing the liquid structure in the hydrogel with a gas to give a dry structure. Hydrogels contain up to 70 % moisture, xerogels 40–50 % moisture and aerogels less than 6 % moisture. Control of the unit operations in processing allows for a wide variety of pore volumes and surface areas, giving a range of activities for differing beers or intended degrees of treatment.

It is worth noting that microbiological contamination of silica gels could lead to "off-flavors" (Rehm, 1974). Dry silica gels generally contain few micro-organisms. The higher the water content of a silica gel, the greater is the possibility of survival and/or multiplication of micro-organisms.

In practice silica gels may be used in various ways:

1. In the body feed filter aid dose stream in conjunction with the normal filter aid: the silica gel will act as a stabilizers well as being an integral part of the filter aid bed.
2. Added into the conditioning vessel
3. As a total replacement for kieselguhr as a combined filter-aid/adsorbent. Trials using silica gels of differing grades for precoats and bodyfeeds have indicated a very good filtration/stabilization performance. The economics look attractive when compared with classical filter aids and beer stabilities are good (Fernyhough and Ryder, 1990). Dose levels are similar to kieselguhrs in this case (100–125 g/hl). It should be noted that hydrogels are non-dusting, non-toxic and give lower disposal problems than do kieselguhrs, as they can be incorporated into animal feeds or dissolved with caustic.

The practice of dosing/filtration using options 1 and 3 above employs the normal kieselguhr filter systems already described.

Polyvinylpolypyrrolidinone (PVPP)

This agent is a solid particulate cross-linked polymer which adsorbs polyphenols and polyphenol-protein complexes. The structure of the vinyl pyrrolidinone repeat unit is shown in Figure 16–10. PVPP was developed by MacFarlane and

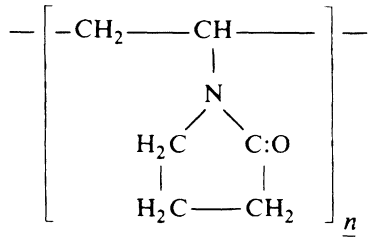


Figure 16–10 PVPP repeat unit.

Bayne in 1961 after initial studies several years earlier (Macfarlane, 1954). PVPP is quite selective in its adsorbing capabilities and even in excess does not adsorb bitter substances. The mechanism of action is thought to be through the formation of hydrogen bonds between the phenolic hydroxyl group and the amide bond of the agent. Table 16–2 shows the effect of PVPP for different types of polyphenol (Dadic, 1973). Improvements to beer taste are said to occur due to PVPP treatment *e.g.* improved quality of bitterness.

The most common procedure for using PVPP is to treat the beer downstream of the kieselguhr filter by dosing a slurry of PVPP ahead of a horizontal leaf filter which then traps the PVPP and forms a bed on the plates. PVPP is also frequently incorporated into filter sheets which can be regenerated with caustic washing (1–2 % caustic). Cartridge filters (wound polypropylene) are often employed downstream to trap any PVPP which bleeds through the plates. This precaution is necessary as PVPP is an elastic deformable material when wetted (Leeder, 1993a). As PVPP can be recycled and recovered, waste is minimized.

A very detailed study (Schafft *et al*, 1979) of many PVPP installations indicated typical performance /operating conditions to be:

1. The PVPP is dosed in typically at between 25 and 50 g/hl.
2. Polyphenols are reduced by 50 %
3. Reduction of anthocyanogen in beer is by 60 %
4. Enhanced colloidal stability
5. Loss of PVPP per cycle (see above) is 1.2 %. The performance of the most modern systems will almost certainly achieve lower losses than this figure.

It has been suggested that care should be taken in using PVPP (and indeed other polyphenol adsorbers) as for some beers (particularly very light and pale beers) excessive use of PVPP can lead to an oxidized flavor due to removal of antioxidant of polyphenols. There is, in these instances, a need to strike the right balance between haze control and flavor stability (Dadic, 1971 and 1984). However, it has also been suggested that although polyphenols do protect against molecular oxygen, for the brewer it is much more important to ensure the exclusion of air in package (Walters *et al*, 1997).

Nylon

This operates on the same principle as PVPP. However there is evidence that nylon gives excessive removal of proteins and is thus not as

Table 16–2 Removal of polyphenols from beer by PVPP (from Dadic, 1973)

	Polyphenols in beer (mg/l)		
Treatment with PVPP (g/60 ml of beer)	*Anthocyanogens*	*Catechin*	*Tanninogens*
1	88	105	193
2	30	5	35
4	20	10	30

From Dadic (1973).

selective as PVPP: head retention and bitterness can both be adversely affected (Dadic, 1973).

Bentonite

These are three-layered clay based on aluminium silicates, $(Si_4O_{10})(AlOH)_2nH_2O$. They swell dramatically in water and are general adsorbents for surface active species. This lack of specificity can have a deleterious impact on head retention values. They have been tested under various laboratory and full-scale conditions. Dose levels of 100 to 200 g/hl are typical and the resultant beers show reductions in total nitrogen of some 22 % and coagulable nitrogen of 86–96 %. Colloidal stability of beers is much improved with the use of bentonites. Contact times between beers and bentonites of 15 minutes to 8 days have been studied. At least 1–3 days is necessary to allow the clays to settle and hence to avoid filtration difficulties. Sediment volumes with bentonites are typically between 1 and 3 %, however figures as high as 10 % have been observed with high levels (300 g/hl) of bentonite (Wolter and Fredder, 1964). Bentonite would normally be added into the conditioning vessel. Practical trials using bentonite in conjunction with other stabilizers such as PVPP have been undertaken. The increased volume of tank bottoms was again observed to be a problem (Narziss and Riecheneder, 1977).

The cider industry has long been a user of bentonites for haze removal during conditioning. The mechanism is not only one of protein adsorption but in this case the ability of bentonites to form loose networks in solution (so called card-house structures) allows enmeshing of colloidal particles and attraction of particles of opposite charge.

Activated Carbon

There is virtually no use of this material in beer treatment, its performance is non-specific and variable between carbon types. It may be used in brewery water treatment systems.

Enzymes

The most frequently used enzyme stabilizers are the proteases, notably papain. Papain is sourced from the latex of papaya, whereas the seldom-used alternatives bromelain and ficin come from the pineapple and fig respectively. Papain operates by reducing the molecular weight of proteins thereby changing their solubility and complexation behavior. The major downside to adding papain, which is usually to conditioning tank or en route to filtration, is that it can have a significantly deleterious affect on foam.

Glucose oxidase has also been proposed for lowering the oxygen contents of beers (Hartmeier, 1979). Both free and immobilized glucose oxidase have been studied, the latter allowing easy removal and reuse. Such enzymes may be incorporated into bottled beer, perhaps immobilized into crown corks. However there is little justification for this enzyme when modern bottling lines are employed which achieve very low oxygen levels.

DILUTION OF HIGH-GRAVITY BEERS

Many beers are produced using high-gravity brewing, where the beer is brewed to and fermented from a higher concentration of wort and then diluted at the end of the process to sales gravity. This process has some disadvantages in beer production. Extra plant is normally required for recycling of weak wort and for de-aeration of dilution liquor. Also, some other problems and inefficiencies are caused. These include the potential for increased production of the flavorsome esters in fermentation and also relatively poor extraction of the hops earlier in the brewing process. The advantages, however, clearly outweigh the disadvantages: there is a much lower plant capacity requirement upstream of the bright beer tank and substantially lower costs of heating in the brewing process and cooling during and after fermentation. The amount of yeast growth per unit of alcohol produced is less in high-gravity fermentation, thus the process is more

"biochemically efficient". There is also reduced requirement for "tank bottoms" recovery. Lesser, but significant, advantages occur in the area of product quality. Provided that the dilution is post-filter, filtration may occur at lower temperature since the elevated alcohol content depresses the freezing point of beer. Also dilution water is completely de-oxygenated so that the oxygen level in the product is lowered by dilution, aiding product stability.

The simplest deaeration plant for dilution liquor comprises a column into which the water is sprayed from the top. An inert gas, generally nitrogen, flows up the column thus de-oxygenating the droplets. Dilution water may also be pre-carbonated if carbon dioxide has been used as the stripping gas, reducing subsequent gas adjustment. The water is collected from the base of the column. Variations on this plant include pre-heating of the water, packing in the column and operation under vacuum.

Blending of high-gravity beer with the dilution liquor is by blending in-line. In-line flow measurement enables automatic control for the specified blend ratio. Alternatively, beers may be diluted to a specified ethanol content by control systems based on in-line or at-line ethanol measurement. Such measurement may be achieved by techniques such as gas chromatography, gas-permeable membrane analyzers, sound velocity monitors (Pfisterer *et al*, 1992) or near infra-red spectroscopy (Proudlove, 1992).

PASTEURIZATION

Introduction

Pasteurization is the most common technique used to reduce the numbers of harmful microorganisms in beer. Two main types of pasteurizer are used: plate (flash) pasteurizers and tunnel pasteurizers. The latter are used mainly for in-pack treatment. Flash pasteurization is used for continuous treatment of beer in bulk for subsequent filling into kegs and occasionally for filling into sterile small pack containers. The theory, equipment, operational aspects and impact on quality will be covered in this section. Reference is mainly to beer but the same principles apply to cider.

Theory

The bacterial "kill" efficiency in pasteurization is determined both by the temperature (T, °C) and the time (t, minutes) for which the beer is held at that temperature. This is defined in terms of pasteurization units (PU):

$$PU = t \times 1.393^{(T - 60)}$$

Typical PU figures found in breweries today are 20 to 30, with t = 20–30 seconds and T between 70 and 75 °C (Hyde, 1986).

This simple equation originates from studies by Del Vecchio *et al* (1951) who studied bacterial survival in a defined mixture of spoilage organisms and identified a thermal death-time curve which predicts combinations of time/temperature which are lethal. However, the survival rate of bacteria for any PU is dependent upon the initial number which are present. The term logarithmic death is used to define a relation between the numbers which are initially present (N_0) and those surviving (N) at time t:

$$N/N_0 = e^{-kt}$$

where k is the temperature dependent specific death rate.

In practical terms it should be noted that pasteurization is *not* a sterilization process but merely reduces the numbers of bacteria. Approximately 2 PU is required to achieve a decimal reduction in bacterial population (Fricker, 1984).

Equipment and Process Conditions

Flash pasteurizers are now available which will cope with variable and constant throughputs (Dymond, 1993). Figure 16–11 comprises a schematic diagram of a modern variable flow flash pasteurizer.

The practice of pasteurization is amply described by O'Connor-Cox *et al* (1991). Four stages of heat exchange are used with a holding

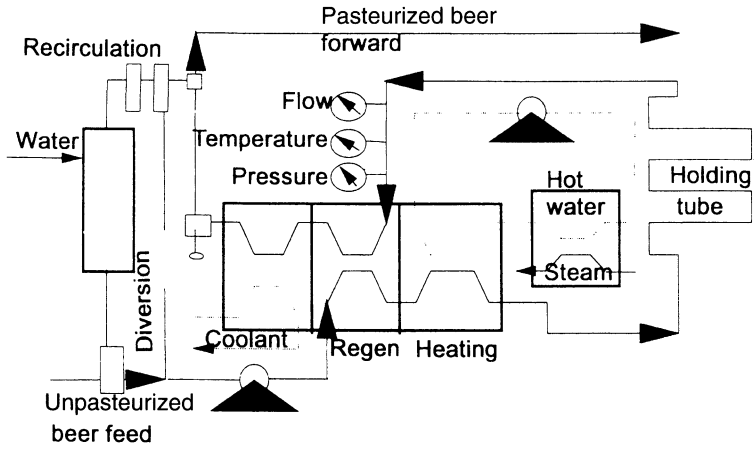


Figure 16–11 Schematic of a variable-flow flash pasteurizer.

tube to give the required residence time. The initial heating of incoming beer (entering at 0–5 °C) is achieved by exchanging heat with the pasteurized beer leaving the unit. This also lowers the temperature of the pasteurized beer, taking the load off subsequent cooling. This is called the regenerative section: the amount of heat recovered is expressed as a percentage of regeneration, "regen". The level of regen used today is between 93 and 97 %. Incoming beer will be raised to about 65 °C and outgoing beer lowered to 15 °C (from 72 °C). Second stage heating is via hot water/beer heat exchange (this water is itself heat-exchanged with steam in a separate section of the pasteurizer). The beer then flows into the holding tube. Residence times are typically between 30 and 60 seconds at 72 °C. Hot beer then flows through the regen section and into a cooling stage which returns the temperature to between 0 and 5 °C. Figure 16–12 shows typical temperature and residence times experienced in a flash pasteurizer.

One implication of the temperature cycle experienced by the beer is that carbon dioxide solubilities change and there is a need to control pressures to prevent gas break-out. If gas break out occurs, heat transfer can be very poor locally leading to survival of organisms. Furthermore, hazes can be induced by protein denaturation at gas/liquid interfaces and foams might be formed, leading to difficulties in fluid pumping. Beer with 5.5 g/L of carbon dioxide at 72 °C will have a pressure of 8.5 bar. Figure 16–13 outlines typical carbon dioxide pressures, plate heat exchange, operating pressures, and temperatures. In order to select pumps etc. and to build in a safety margin, it is normal to design the system to run at 3–4 bar above the saturation pressure.

If plates become cracked or seals degrade in the regen section then the opportunity exists for unpasteurized beer (normally at higher pressure than outgoing beer) to mix with pasteurized beer. To control this, four-yearly plate inspection is typically undertaken. Nowadays, a boost pump is often fitted ahead of the regen section on the pasteurized beer side to maintain a greater pressure on this side. Then any beer flow across damaged plates will be from a pasteurized to a non-pasteurized stream.

Flash pasteurizers are available in different configurations and operating modes, dependent upon the brewery operation. Modern filling lines demand variable flow rates of beer as a consequence of packaging operations. It is expected

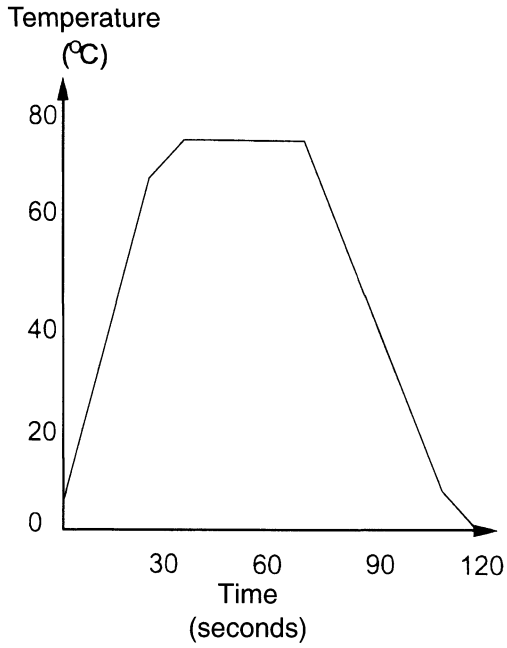


Figure 16–12 Temperature and residence times in a typical flash pasteurization process (after Dymond, 1993).

that modern pasteurizers maintain efficiency irrespective of flow rate. This is achieved with sophisticated microprocessor control: the software automatically adjusts the pressure control system thereby maintaining the correct holding tube pressure and preventing gas break-out. The pressure drop in a pasteurizer is directly proportional to the square of the flow rate.

Tunnel pasteurizers are used for "in-pack" pasteurization. After cold-filling and sealing of the containers, product preservation (heating up, temperature holding, cooling down) is carried out by heating the packs and contents. The packs are conveyed on a moving belt through various zones in which water is sprayed at a range of temperatures. Spray water flow, temperature and product residence time are controlled. For reasons of energy conservation, a twin deck design is often used in which water from an upper deck cascades down onto a second lower deck to maximize water and heat efficiency. The water is again regenerated by exchanging incoming cold water with hot exit water which is collected in sumps in various zones (Huige *et al*, 1989).

Effect Upon Beer Quality

Pasteurization has been implicated in changes in the nature of beer. This is mainly attributed to the presence of oxygen, with the high temperatures leading to rapid reactions and flavor changes. Haernluv and Larsson (1992) highlighted this effect when comparing pasteurization with membrane filtration. If O_2 levels were allowed to increase above 0.7 ppm then chill hazes became apparent on prolonged storage tests. Mallet (1988) has recommended that O_2 levels should be less than 0.3 ppm. Narziss (1986) has shown that with long treatment times (30 minutes as compared with more normal times of 60 seconds), as might occur with interruptions in filling in some constant speed fixed flow pasteurizer configurations, aromas and bitterness deteriorate. Chemical analysis has indicated that N-heterocycles also increase.

COLD STERILIZATION OF BEER

This alternative to pasteurization relies on fine filtration to significantly reduce levels of spoilage organisms. The main driving force behind this technology has been market differentiation of products and the elimination of subtle, but adverse taste changes imparted by pasteurization. Often, as in pasteurization, not all organisms are removed, but the numbers remaining are not significant for decreased biological stability within typical product shelf-lives. Costs of cold filtration, compared to flash pasteurization, are favorable when new plant options are being considered, particularly so for small plant (Leeder, 1993b).

There are many plant and operating options which will achieve cold sterile-filtered products. They all rely on a cascade type approach, where sequentially finer stages of filtration are

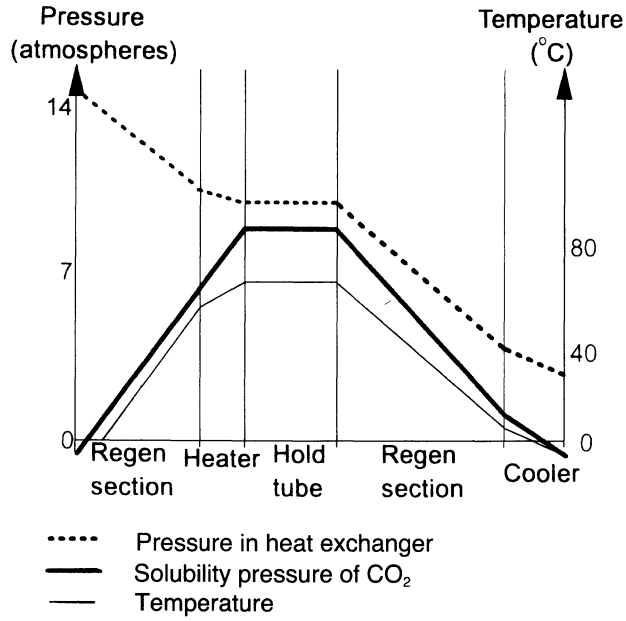


Figure 16–13 Carbon dioxide pressures within a flash pasteurizer.

used ahead of packaging. The most common sequences are:

Kieselguhr filter ---- sheet filter
Kieselguhr filter ------- PVPP sheet filter ------- fine membrane filter
Kieselguhr filter -------- multi-layer graded depth filter (the Multi micro system) (Gaub, 1993)
Kieselguhr filter ---------- ceramic filter (Beer, 1989).
Kieselguhr filter ---------- first stage membrane cartridge filter ---------- second stage membrane cartridge filter (Ducheck, 1993).

Some systems are still more complex and have been in operation for some time. Figure 16–14 shows the system in operation in Coors which is based on Enzinger fibrous mass dosing filters, sheet filters and kieselguhr filters (Mefford, 1990). Figure 16–15 shows the diversity of Kirin systems which are based on filter aid filtration, sheet filters and membrane cartridge filters (Takahashi *et al*, 1990).

There follows a brief description of the most common filter types used downstream of a kieselguhr filter.

Sheet Filters

These are generally made of cellulosic fibres which have been compressed into a thin mat. Some may employ resins to bind them and there are also options to include PVPP within the structure so that colloidal stability can also be enhanced. Sheets impregnated with kieselguhr are also available and if the content of kieselguhr is graded throughout the sheet to give higher voidage on the inlet rather than the outlet then overall performance is enhanced. Sheet filters are installed within plate and frame devices. Sheets are regenerated by backwashing but must be replaced every few months. Because of the low permeability of the sheet material and the need for low pressure drops in series, surface loadings are generally low, typically 1 hl/m^2 per hour. A range of sheet grades is available with differing degrees of filtration performance.

Enzinger Pulp Filters

This filter consists of pads of cellulosic fibre which are run in parallel. The pads are typically 500 mm in diameter and 40–45 mm thick and

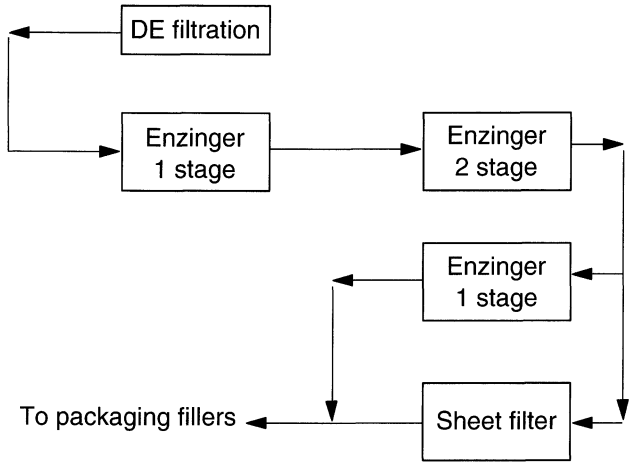


Figure 16–14 Coors cold filtration system (Mefford, 1990; reproduced courtesy of the European Brewery Convention).

are held in circular filter plates. The pulp pads are not backwashed as this would break them up. Rather the pads are pulped in water after which the cellulose is washed and reformed for reuse (Beckett, 1985).

Cartridge (Membrane) Filters

These are small units enclosing a filter element. For brewery applications, the most common types employed are membrane and depth filter cartridges. Depth cartridge filters are often made of porous polypropylene, teflon, or glassfibres and comprise typically elements some 25 or 50 cm long with a few cm of media.

Membrane filters act as absolute barriers with a well-defined pore size (typically cut-offs of 0.45 to 0.8 microns are used). They are very sensitive to blinding as they are surface filters. It

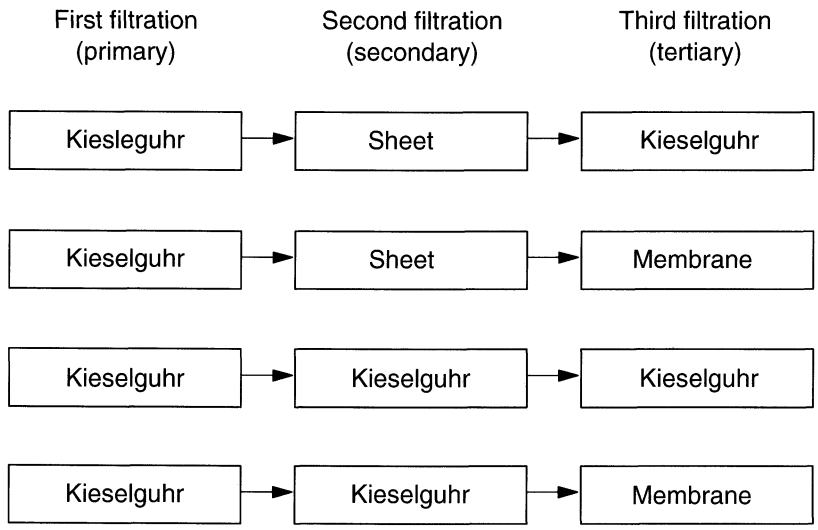


Figure 16–15 Kirin cold filtration lines (Takahashi, 1990; reproduced courtesy of the European Brewery Convention).

is common to have these filters downstream of both kieselguhr and sheet filters in order to maintain an adequate lifetime. The active membrane filtering layer is often 100 microns thick and may be on a support. The membrane filter is generally pleated around a central "former" to give a very large surface area. Membrane materials are typically polytetrafluoroethylene, nylon or polypropylene. Membrane cartridges in the final stage offer many advantages in that they can be simply integrity tested after cleaning to ensure their bacterial filtration capability is not impaired (Roast, 1991).

Ceramic Candles

These are cylindrical filter elements made of pure aluminium silicate, typically with a wall thickness of some 25 mm (Beer, 1989). They are usually precoated with kieselguhr at the start but no bodyfeed is used. Capacity is typically 10 hl/m^2 per hour.

GAS ADJUSTMENT

In the modern beverage plant dissolved gas levels often need to be adjusted. If ales or stouts, which frequently have relatively low carbon dioxide specifications, are fermented in large cylindroconical vessels then the hydrostatic pressure towards the base can cause higher levels of carbon dioxide than required and decarbonation is necessary. Conversely high carbonation small-pack and draught beers may require extra carbonation. Some products are pressurized with a mixture of carbon dioxide and nitrogen. The result is a product with sufficient top-pressure of gas but a lower carbon dioxide loading. Nitrogen is found to have benefits in terms of foam quality and "mouthfeel" (Kennedy, 1994 and Taylor *et al*, 1992).

Should extra carbonation be required, the simplest method is to carbonate in-line, generally after the filter. Carbon dioxide is injected into the flowing beer main through a sinter resulting in a stream of bubbles in the beer. Mass transfer effects for this operation are explained by the application of Henry's Law and the laws of diffusion:

$$C_e = H.p_e$$

where C_e is the equilibrium concentration of carbon dioxide in beer (kg/m^3); p_e is the equilibrium partial pressure of carbon dioxide on the beer (Pa) and H is Henry's Law Constant ($kg/m^3/Pa$)

$$\frac{dC}{dt} = k.A.(C_e - C)$$

where dC/dt is the rate of change of concentration of carbon dioxide in the beer (C) with respect to time t ($kg/m^3/s$); k is the mass transfer coefficient ($/s.m^2$); and A is the mass transfer area (m^2).

Henry's Law relates the equilibrium partial pressure (Atkins, 1982) of a gas to its dissolved concentration in a liquid. Gaseous and aqueous phases of CO_2 can take a long time to equilibrate, thus sparkling beverages take a few hours to go flat after dispensing. Henry's Law constant (H) is very temperature dependent, and H is higher at lower temperatures due to increased gas solubility. Values of H for beer are very similar to those for water (Sellés, 1990).

The second equation illustrates why certain process conditions outlined below are employed. Rapid solution of CO_2 is achieved:

- under high pressure so that C_e is higher. Ideally the pressure of the gas stream is significantly higher than that of the beer stream
- using a stream of fine bubbles from a sinter so that A is high
- in conditions of very turbulent flow; the gas is normally introduced into a narrowed pipe bore, which causes the mass transfer coefficient k to be higher
- injection into a long main so that the solution time t is as great as possible

Decarbonation of beverages is a substantially greater problem than is carbonation. Purging with inert gas is necessary. The bulked beverage is run into a tank which has a facility for sparging through a sinter at the base. In the case of

beer, such processing has a detrimental effect on product quality: foam is generated which reduces the head potential of the dispensed product, and unsightly suspended "bits" may also be produced.

One possible alternative is the use of hydrophobic membranes. Some polymers such as polytetrafluoroethylene, polypropylene or polyvinylidenefluoride are hydrophobic (low wettability by liquids). A membrane constructed from these materials, with pore sizes below approximately 0.2 microns, will not pass liquid within reasonable pressure limits, whereas it is permeable to gases (Bühler *et al*, 1993). There is therefore the potential, given enough contact time with the membrane, for the beverage to decarbonate to the required level. Such a system has no adverse effect on product quality and no requirement for other purge gases. Importantly, different gases may be transferred across the membrane independently of each other. Hence, decarbonation may be performed simultaneously with nitrogenation. A reduction in dissolved oxygen levels would also be expected. Such systems are commercially available (Gill and Menneer, 1997).

Systems for the recovery of carbon dioxide from fermentations or from inerting operations for use later in the process are becoming more common. As well as being economically viable in large operations, clearly the recycling of a "greenhouse gas" has environmental benefits. Systems consist of collection and cleaning with water scrubbing, drying with alumina and purification with activated carbon prior to compression and liquefaction (Gruber, 1975).

CASK ALES

These are produced in substantial volumes in the U.K. Their feature is the employment of secondary fermentation in the final container.

Fermentation is traditionally in shallow vessels, using a top fermenting yeast. Yeast is skimmed from the top of the beer, and primary fermentation effectively ends when the yeast loading remaining in the bulk beer falls to a specified value (2×10^6 cells/ml or less). The beer is then racked and through addition of priming sugars a secondary fermentation is induced. Racking is performed via a racking back (Figure 16–16) which has provision for pressurizing of itself and the casks and collection and return of fob during filling.

Priming sugars are added as syrups, perhaps to 1 % of the beer volume. Isinglass finings are also added to a similar volume, essential to settle the solids in the cask and clarify the product for satisfactory presentation to the consumer. Isinglass finings consist of high-molecular-weight collagen molecules which are typically manufactured from the swim-bladders of tropical fish (Leach and Barrett, 1967).

There are also several optional additions. "Dry hopping" entails addition of a plug of whole hops or hop pellets, to impart extra hoppy character to the beer but not bitterness. Alternatively, hop extracts may be added. Color may be added in the form of caramel or malt extract. Biocides such as sodium metabisulphite may be added at levels which do not impinge on beer flavor.

The beer is held at the brewery for the period of the secondary fermentation, *e.g.* one week. The fermentation temperature used is akin to the warm conditioning period used in some lager beers, *e.g.* 15 °C. Gas produced in the cask is vented by the use of spiles in the cask inlet. Spiles are selected on the basis of their permeability to gas flow, such selection forming the basis of control of CO_2.

Dispense is enabled by driving a tap into the cask outlet (a second hole). The cask must then be left for a day or more for the finings to cause all solids to settle into the belly of the cask. The cask is positioned on its side, and full removal of the clear beer is enabled by gradually tilting the cask during dispense.

BEER RECOVERY

The solid residues from the fermenter and conditioning stages are, like the beer, valuable

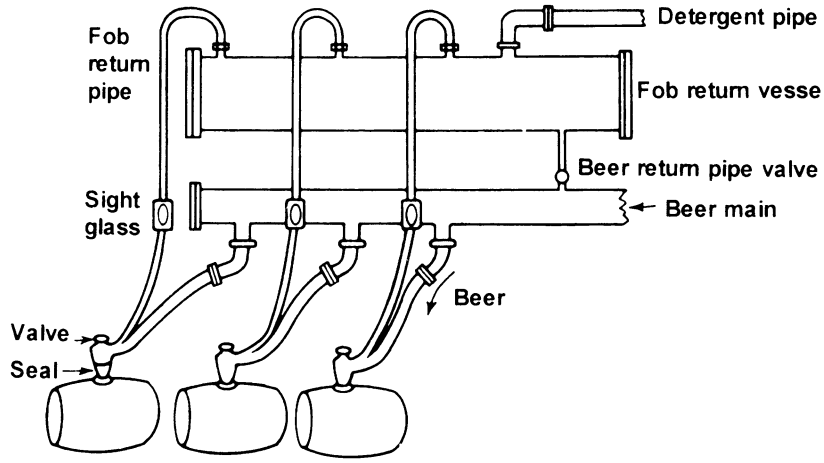


Figure 16–16 Racking back for the filling of casks (courtesy of Chapman and Hall).

product streams. The quality of the beer and condition of the yeast are vital to ensure maximum value. Three forms of waste yeast slurries are most usually available for treatment (Young, 1985):

- Yeast slurry from fermenters (8–15 % dry solids).
- Centrifuge discharge from those plants which use this step between fermenters and conditioning vessels
- Conditioning vessel bottoms (2–7 % dry solids comprising yeast and chill haze complexes)

Many processes are used for recovering product from tank bottoms (Loveridge, 1992):

1. Centrifuges
2. Vacuum filters
3. Filter press and pressure leaf filters
4. Alcohol evaporation systems
5. Crossflow membrane filtration

1. Centrifuges

Centrifuges used for beer recovery are usually disc bowl/disc stack types. They are most often used for thickening fermentation vessel yeast but have in the past had severe limitations in preparing final cake solids, producing a paste which is difficult to handle. They often have a high power consumption and, hence, running cost. Centrifuges may be used in transfer to conditioning vessel from fermentation: 98–99 % of the yeast may be removed to give a discharge of 25 % yeast (dry weight). The characteristic feature of this type of centrifuge is the stack of conical discs, the spaces between which are about 0.5–2 mm and the cone angle 30–50 ° (Figure 16–17). Feed is introduced into the bottom of the bowl and is deflected into the annular space between the bowl and the wall and the outer edge of the disc stack. It then flows through the stack to the outlet at the top. Yeast cells move horizontally through the liquid until they encounter the sloping surface of a cone, they then slide down and are collected on the walls of the bowl. Continuous operating designs are now commonplace, with automated solids discharge. Entrance and exit configurations can vary and both top and bottom entry are now commonplace. Decanter centrifuges have also been assessed for recovery of fermenter bottoms, although these are generally not as efficient.

2. Vacuum Filters

Vacuum filters consist of a rotating drum (*e.g.* wedge wire) which may be precoated with

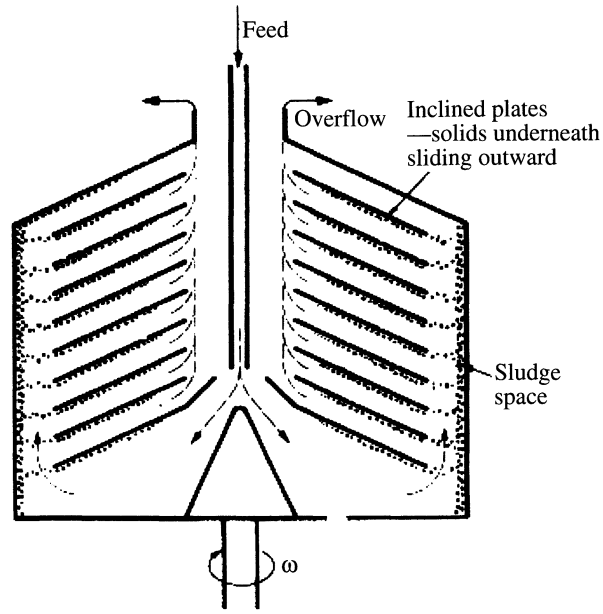


Figure 16–17 Internals of a disc stack centrifuge (from Murray, 1993).

kieselguhr and then immersed in tank bottoms (Figure 16–18). The drum is normally rotated such that it immerses in the stream to be treated over a small part of its circumference, with the vacuum applied from the centre of the drum. Options are available for scraping off the formed cake or for washing. Vacuum filters are less common than they once were because of the inevitable pick-up of oxygen.

3. Filter Presses

Filter press recovery is one of the commonest approaches. Diaphragm yeast presses are used for beer recovery from fermenter tank bottoms. Both yeast presses and horizontal leaf presses are used for conditioning vessel bottoms. Fermenter yeast comprises 40–60 % spun solids and normally consists of healthy yeast free from autolysis and suitable for re-use. In fermenter tank bottoms the yeast can be concentrated up to 30 % (dry weight). It is common practice to add filter aid to conditioning tank bottoms to improve deliquoring as these are more problematical to treat being only 20–40 % by weight of spun solids and they may contain a high proportion of protein. Careful consideration is demanded for disposal of the solids generated from these plate and frame systems. If a powder press is used then the only option is landfill. If a yeast press is used then options are open for both animal feed and distillation to recover alcohol.

4. Alcohol Evaporation Systems

Alcohol evaporation systems involve heating the slurry (30 °C) while it is falling through tubes (as in a shell and tube heat exchanger) under partial vacuum (Figure 16–19). Evaporation of 40 % is typical and the vapor is separated from the solids in a cyclone separator (Johnstone, 1990). The beer volatiles are typically blended back into mainstream cellar tank beer after filtration through activated carbon. The solids or yeast slurry contains lysed cells and is most commonly sold into animal feeds. Up to 18 % alcohol concentration is typical.

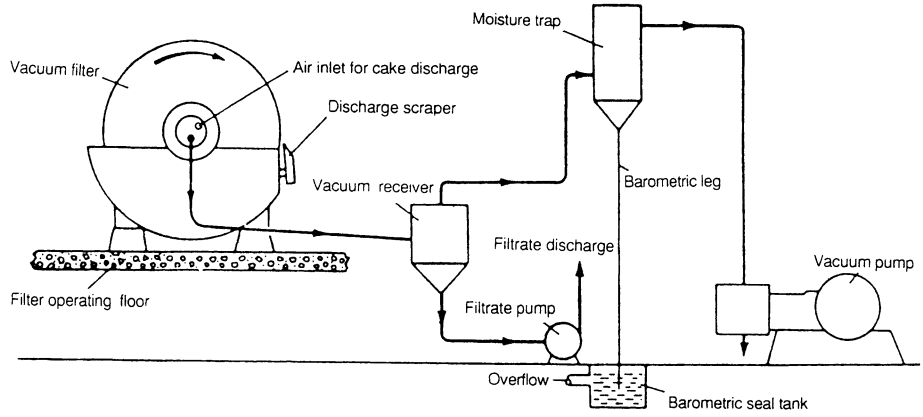


Figure 16–18 Rotary vacuum drum filter (Coulson & Richardson, 1977; courtesy of Butterworth–Heinemann).

5. Crossflow Membrane Filtration

Crossflow membrane filtration was outlined briefly at the end of the section on filtration. The technology has become accepted of late as a treatment for tank bottoms (Ryder *et al,* 1988; Girr and Leeder, 1992). This technique is also commonly applied to the treatment of cider tank bottoms where the nature of the fluid and the temperatures of processing (typically 30 °C) means that the fouling is less severe and a high quality product can be obtained.

A configuration for a tank bottoms treatment plant is shown in Figure 16–20.

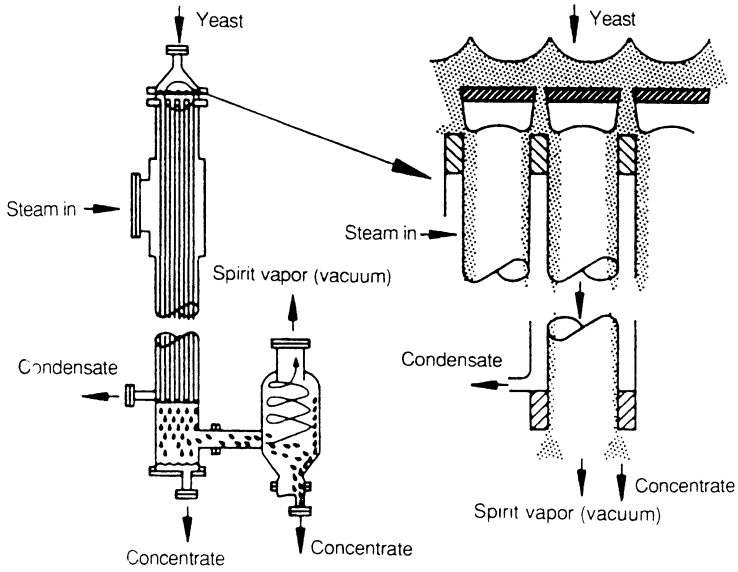


Figure 16–19 Alcohol evaporation recovery system (Johnstone, 1990; reproduced courtesy of the European Brewery Convention).

THE FUTURE

One of the most pressing developmental needs in the area of brewery processing is the need to look for viable alternatives to kieselguhr, the use of which is under pressure due because of environmental concerns over handling and, more importantly, disposal in land fill sites. The use of crossflow membrane technology for mainstream rough beer clarification is most likely to replace diatomaceous earth filters once the fouling of membranes and product quality issues have been resolved. Stability will continue to be of prime importance and new stabilizing aids will continue to be developed. The stabilizing procedures will need to take account of raw materials which will continue to diversify and will impact upon beer stabilization. Rapid throughputs in cold maturation and the ability to handle many differing brands will dictate the shape of many brewery processes. Waste minimization, energy and water conservation and effluent treatment will also play an important role in the future in dictating the format of processes. Continuous fermentation is being revisited which will require different downstream processing. A brief discussion of future scenarios has been given elsewhere (McKechnie, 1993).

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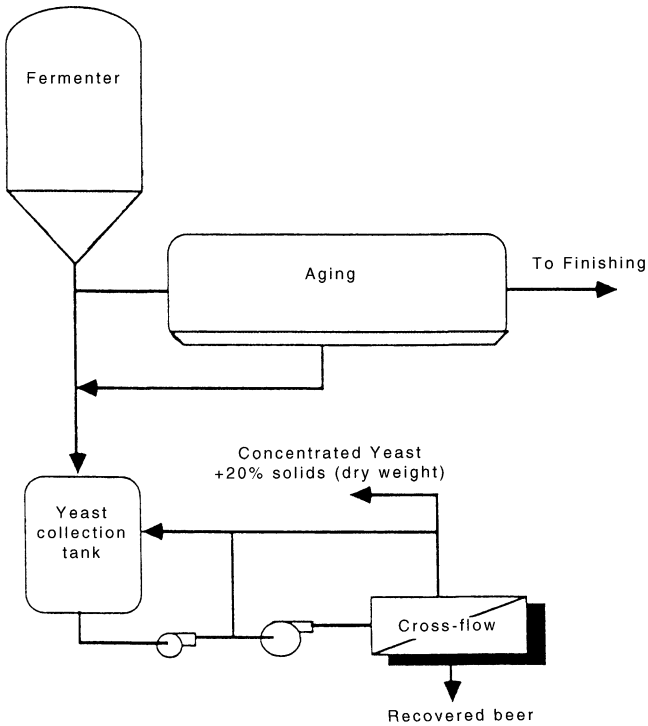


Figure 16–20 Cross-flow microfiltration plant for treating tank bottoms (Ryder *et al.*, 1988)

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17

Flavor Chemistry

V.C. Cole and A.C. Noble

INTRODUCTION

The distinctive flavors of beer, wine, and distilled or fortified alcoholic beverages are affected by many variables: raw material, flavor additives, and processing steps, which include fermentation, distillation, and subsequent aging. In this chapter on the flavor chemistry of alcoholic beverages, the most important contributions of raw material, processing, and aging are surveyed for beer, wine, and distilled spirits.

Over 1,300 volatile compounds have been identified in alcoholic beverages (Nykänen, 1986). In one study alone, 213 compounds were identified from the juice of Sauvignon blanc grapes (Sefton *et al.*, 1994). With few exceptions, perceived flavor is the result of a pattern or specific ratios of many compounds, rather than being attributable to one "impact" compound. The major products of fermentation in alcoholic beverages are esters and alcohols, which are present in high concentrations. These typically contribute only a generic background flavor, whereas the distinctive aroma notes are usually elicited by many trace compounds. Since so little is known about which compounds contribute to the distinctive aromas of these beverages, this chapter focuses on the volatiles that have been shown to contribute to specific flavor characteristics and surveys the effects of specific processing steps.

RAW MATERIALS

Wine Derives Flavor from Grapes

Despite advances in methods for isolation and identification of compounds present in *Vitis vinifera* wines, only in a few cases have specific compounds been identified that are responsible for characteristic varietal flavors. In contrast, the distinct "Concord grape aroma" of *Vitis labrusca* grapes and wines is due largely to methyl anthranilate, methylfuraneol, and *o*-aminoacetophenone (Shure & Acree, 1994). Lists of volatiles identified in wines, as reviewed elsewhere (Schreier, 1979; Rapp & Mandery, 1986), are dominated by compounds that are products of fermentation. The trace components, which often confer the varietal distinctiveness and come from the grape, require extensive enrich-

ment for recovery in amounts required for detection and identification.

Grape variety, viticultural practices, climatic conditions, soil, and region of origin affect vine development and berry composition and exert major influences on distinctiveness of wine flavor, as evaluated by sensory descriptive analyses (Elliott-Fisk & Noble, 1991; Fischer *et al.*, 1999; Guinard & Cliff, 1987; Heymann & Noble, 1987; Noble, 1984; Noble & Shannon, 1987; Ohkubo *et al.*, 1987). Despite this, only for a limited selection of grape varieties have the compounds that produce these distinctive aromas been identified. Terpenes in the aromatic varieties and alkoxypyrazines in the vegetative or herbaceous cultivars are examples of impact compounds arising from grapes that contribute to the characteristic aromas of the wines. The varietally distinct flavor notes, such as berry aromas in Zinfandel (Noble & Shannon, 1987), Cabernet Sauvignon (Heymann & Noble, 1987), and Pinot noir (Guinard & Cliff, 1987), or black pepper notes in Zinfandel (Noble & Shannon, 1987), have been quantitatively evaluated in sensory tests. No impact compounds have yet been identified, however, that elicit these aromas in wines.

One class of compounds that elicit distinctive floral aromas in "aromatic" *Vitis vinifera* varieties (Muscat, Gewürztraminer, and Riesling) is terpenes. Over 60 monoterpene compounds have been identified in Muscat grapes and wines, of which the most abundant are geraniol, linalool, and nerol. Lower amounts of citronellol, nerol-oxide, α–terpineol, diendiol-I, and various forms of linalool oxides have also been found (Strauss *et al.*, 1986). Over 90 % of the total terpene content occurs in a nonvolatile form, however, with the terpenes bound to sugar molecules. As first proposed by Williams and coworkers (1982), these glycosides serve as flavor precursors in floral varieties. Terpenes released by hydrolysis from Muscat glycosides increased the floral aroma of wines to which they were added, which demonstrates the sensory importance of these flavorless terpene glycosides in Muscat varieties (Noble *et al.*, 1987). The distinctive aroma of Gewürztraminer has been more narrowly attributed to the presence of *cis* rose oxide, β–damascenone, and linalool, all liberated by hydrolysis from glucosides (Guth, 1997a, 1997b; Ong & Acree, 1999).

In general, levels of both the free and bound terpenes increase with light exposure (Razungles *et al.*, 1998; Reynolds & Wardle, 1992) and as grapes ripen (Park *et al.*, 1991; Wilson *et al.*, 1984, 1986). Thus, managing vineyards to increase light exposure in the fruiting zone and harvesting grapes at high maturity levels will yield the highest concentration of total terpenes. Extraction of the terpenes and their glycosides from grape skins can be increased by using extended skin contact or higher pressures during pressing (Kinser & Schreier, 1980). Enzymatic hydrolysis of these odorless precursors has been proposed as a step in winemaking. Despite extensive surveys, no glycosidases were found that were active above 1–2 % sugar, although several were isolated that were effective in wine (Aryan *et al.*, 1987; Shoseyov *et al.*, 1990). Terpene glycosides hydrolyze slowly in grape juice or wine due to acid catalysis (Park & Noble, 1993). The very high acidity of the wine used to make brandy is thought to result in a more flowery brandy than if grapes with lower acidity at higher maturity were used for wine for distillation (Strauss & Williams, 1983).

Unlike in the aromatic varieties, very low levels of terpenes are found in Chardonnay (Dimitriadis & Williams, 1984; Sefton *et al.*, 1993a) except in an Italian clone (Versini *et al.*, 1988). In nonaromatic white varieties such as Chardonnay, Sauvignon blanc, and Semillon, glycosides of 13 carbon (C_{13}) norisoprenoids, including theaspiranes, vitispiranes, and β–damascenone, have been found (Sefton *et al.*, 1989a; Sefton *et al.*, 1993b; Sefton *et al.*, 1994). Over 70 % of Chardonnay glycosides have norisoprenoids as the aglycone (Sefton *et al.*, 1993b), many of which arise from degradation of carotenoids (Williams *et al.*, 1992; Winterhalter, 1996). The potential of nonterpene glycosides to serve as flavor precursors has been confirmed in three white grape varieties. Hydrolysis of Chardonnay

or Semillon glycosides increased tea, floral, lime, honey, oak, talc, and pineapple aromas. Addition to wine of aglycones released by hydrolysis from glycosides in Sauvignon blanc increased the tea, oak, honey, and lime notes but did not change the distinctive asparagus and bell pepper aromas characteristic of Sauvignon blanc (Francis *et al.*, 1992b).

In red grape varieties, most of the aglycones are norisoprenoids/norterpenoids that are derived from carotenes (Razungles *et al.*, 1998; Winterhalter, 1996). Light exposure of the berries increases the level of these carotenoid derivatives as demonstrated in the Syrah variety. Exposure of berries to sunlight before veraison increased the carotenoid level, and exposure after veraison accelerated the degradation of these pigments (Razungles *et al.*, 1998). The compound β-damascenone (a carotenoid metabolite), which arises from a glycosidic precursor, is ubiquitous in red varieties and has been reported in Cabernet Sauvignon, Cabernet Franc, Merlot, Grenache, and Pinot noir (Kotseridis *et al.*, 1999) as well as in several whites. In red grapes, hydrolysis of glycosides also contributes significantly to wine aroma, although the aromas are not varietally distinct as in the aromatic white varieties. Aglycones released from glycosides of Shiraz grapes increased stalky, earthy, cigar, and tobacco aromas of wines to which they were added. Only in one fraction was the characteristic black pepper aroma of the Shiraz wines sensed by gas chromatography–olfactometry, but no compound responsible for this odor was identified (Abbott *et al.*, 1991). Hydrolyzed glycosides of Cabernet Sauvignon and Merlot increased the intensity of dried fig, tobacco, and chocolate aromas of the respective wines (Francis *et al.*, 1996).

The bell pepper aroma of Sauvignon blanc and Cabernet Sauvignon wines, often described as "herbaceous" or "vegetative," led to speculation that 2-methoxy-3-isobutylpyrazine (MIBP) was present in these varieties (Bayonove *et al.*, 1975). MIBP had been identified previously as the impact compound in bell peppers by Buttery and colleagues (1969). With the use of isotopically labeled pyrazines and selective ion monitoring mass spectrometry (Harris *et al.*, 1987), MIBP was conclusively identified and quantified in Sauvignon blanc and Cabernet Sauvignon wines (Allen *et al.*, 1991; Lacey *et al.*, 1991). The level of MIBP in berries was found to be highest at veraison and in grapes from cooler climates (Allen *et al.*, 1991; Lacey *et al.*, 1991).

Consistent with the observation that MIBP photodegrades at low light intensity (Heymann, *et al.* 1986), Cabernet Sauvignon grapes and wines produced from shaded vines were described as more vegetative than those with more open, unshaded canopies (Morrison & Noble, 1990). In a similar experiment with Sauvignon blanc, light exposure in the fruiting zone was increased by leaf removal, which resulted in a decreased intensity of vegetative wine aromas (Arnold & Bledsoe, 1990). Cabernet Sauvignon vines that had a low level of light in the fruiting zone produced wines that had more intense vegetative (bell pepper) aroma and contained higher levels of MIBP (40 ppt) than wines from vines with more light exposure, which contained 4 ppt MIBP (Noble *et al.*, 1995). The site and path-way for synthesis of MIBP or the isopropyl derivative that is also found in grapes and wines are unknown.

A volatile sulfur compound (4-mercapto-4-methyl-pentan-2-one, or MMP) that produces an aroma described as "boxwood" or "cassis bud" (or cat urine) has been identified in Sauvignon blanc wine (Darriet *et al.*, 1993) and in Scheurebe wine (Guth, 1997a, 1997b). More recently, 3-mercaptohexylacetate, which is also described as having a boxwood or broom flower aroma, was identified in Sauvignon blanc (Tominaga *et al.*, 1996), Merlot, and Cabernet Sauvignon wines (Bouchilloux *et al.*, 1998). The distinctive Sauvignon blanc herbal, boxwood aroma increases during fermentation, as these potent thiols (MMP and 3-mercaptohexanol) are released from their *S*-cysteine conjugate precursors upon yeast degradation (Tominaga *et al.*, 1998).

Nonvolatiles from grapes have an extremely important influence on wine taste and mouth

feel, as well as on the potential for aging (Noble, 1998). Grape acids, tartaric and malic, decrease as grapes ripen. Their levels in grapes are determined by climate, cropping load, and maturity at harvest. Final levels in wine are also influenced by wine processing and aging.

Bitterness and astringency in wines are produced in large measure by tannins (flavonoid phenols) that are extracted from grape skins and seeds (Noble, 1998). Extended skin contact during fermentation can result in phenolic levels of over 3,000 mg/l (expressed as gallic acid equivalents) (Singleton & Noble, 1976). Aging of red wines, whether in barrel or bottle, is associated with a decreased astringency or "mellowing" of the wine due to polymerization of tannins. The large polymerized tannins formed by slow oxidation over time eventually become insoluble and precipitate out of solution, which results in lower astringency in an aged wine. The relative astringency and bitterness of tannins vary primarily as a function of degree of polymerization. Monomers are more bitter than astringent, but as tannins polymerize, astringency increases more than bitterness. Stereochemistry also plays a part; hence, the 4–6 linked catechin-catechin procyanidin dimer is more bitter and astringent than is the 4–8 linked analogue. The nature of the linking unit (catechin or epicatechin) also affects the relative astringency (Peleg *et al.*, 1999; Robichaud & Noble, 1990).

Beer, Whisky, and Gin Derive Flavor from Grain

Wine is fermented from grape juice, whereas beer is fermented from sugars in germinated grains (wort). Both beer and wine share some common sensory characteristics due to the products of fermentation that they hold in common: ethanol, esters giving fruity characteristics, aliphatic acids, higher alcohols, sulfur compounds, acetaldehyde, and so on. In the production of beer, barley is germinated (malted), crushed, extracted with hot water (mashed), and boiled with hops to produce wort. The flavor of beer and its distillates differs from that of wine and its distillates largely due to enzyme-induced changes that occur during malting, as well as thermally induced changes occurring during malt kilning and wort boiling. While over 800 volatile constituents have been identified in beer, few compounds responsible for the distinctive flavor notes have been identified. The temperature and length of time that malt is heated during kilning, as well as the moisture content of malt, affect the level and composition of flavor compounds that are formed. Many flavor components are chemically transformed during wort boiling or during fermentation (Meilgaard & Peppard, 1986).

The malty, caramel, grainy, nutty, and bready aromas characteristic of beer arise by three routes during the processing of grain prior to fermentation. Most volatiles are formed via enzymatic and chemical oxidation of unsaturated fatty acids. During malting of cereals, lipoxygenase and other enzymes act on unsaturated fatty acids to form oxygenated products, which are transformed chemically and thermally during kilning. Some of these volatiles contribute to "green" or grainy aromas, or serve as precursors to oxidized beer aromas (Tressl *et al.*, 1983).

Free amino acids increase enzymically during malting and then undergo Strecker degradations to form corresponding aldehydes, which may themselves have malty aromas or may react with reducing sugars during the heat of kilning (Tressl *et al.*, 1983) or boiling (Meilgaard & Peppard, 1986) to form Maillard products having caramel, cereal, nutty, or corny/bready aromas. Maillard products include pyridines, pyrazines, and pyrrolines, which produce toasted, vegetative, and nutty aromas, and cyclic derivatives such as furaneol, isomaltol, and maltol, which contribute to toffee, caramel, or burnt sugar aromas in beer (Meilgaard & Peppard, 1986). Maillard products of proline include pyrroles, which are particularly important in cereal, bread, or corn flavors (Meilgaard & Peppard, 1986; Tressl *et al.*, 1983).

The degree to which Maillard products form depends on the temperature and moisture content during kilning and accounts for many of the

sensory differences in aroma among beer types. Ales have more Maillard products than lagers because their malts are kilned at higher temperatures. Amber, chocolate, and black malts are kilned at sequentially higher temperatures, which affects the number of Maillard products that they contribute to beers (Meilgaard & Peppard, 1986). Most Maillard products are not transformed by yeast and are found in beer (Hough *et al.*, 1982).

The primary cause of bitterness and astringency in beer is the flavonoids, including catechins and anthocyanogens and their polymers, which are extracted from grains and hops. In addition, bitterness is contributed by iso-α-acids from hops (Meilgaard & Peppard, 1986; Rosculet, 1971). Other bitter-tasting compounds can arise from the reactions of proline and other amino acids during roasting (Tressl *et al.*, 1983).

S-methyl methionine, formed by enzymatic reactions during germination, decomposes to dimethyl sulfide (DMS) during kilning (Tressl *et al.*, 1983) and boiling (Hough *et al.*, 1982). DMS is a major flavor compound in many lager beers, where it is found at levels of 30–70 ppb, adding a cooked cabbage/asparagus aroma note. Cinnamic and benzoic acids found in cereals are transformed into vinyl phenols during kilning and other high-temperature processing phases of beer (Meilgaard & Peppard, 1986; Tressl *et al.*, 1983). These phenols contribute smoky, phenolic, or spicy aromas and play a role in the smoky aroma of malt whiskies. During the boiling of wort, the concentrations of these aroma components rise, as do concentrations of hydroxymethylfurfural, furfural, and 5-methylfurfural (Hough *et al.*, 1982), which produce baked, caramel notes.

Flavor Additives: Hops in Beer

Hops are of such central importance to the flavor of beer that unhopped beer is claimed to taste like an "ethanolic unsweetened lemonade" (Verzele, 1986). Hops added to wort during the boil contribute bitterness to beer due to the extraction of isoprenoid hop resins, particularly the α-acids. During wort boiling these isomerize to the bitter iso-α-acids, which are humulene derivatives. Oxidation of hops during storage can yield more bitter oxidation products (Meilgaard & Peppard, 1986).

Hop essential oil contains over 200 components, including many terpenes, as well as esters, ketones, alcohols, cyclic ethers, acids, and sulfur compounds (Meilgaard & Peppard, 1986). About 75 % of the oil is comprised of the terpenes β-myrcene, α-humulene, and β-caryophyllene (Meilgaard & Peppard, 1986; Verhagen, 1988). The terpenic composition varies with hop variety. Minor terpenes in hop oil that contribute to hop aroma include linalool, geraniol, β-ionone, and β-damascenone. Hop essential oil is not retained if hops are added at the beginning of the boil. If hops are added toward the end of the boil, a more floral character is produced; if they are added after fermentation (dry hopping) more spicy, resinous beer results (Meilgaard & Peppard, 1986). Humulene oxidation products, sesquiterpenoids, appear to cause the "hoppy" aroma, while the monoterpenes linalool and geraniol provide the floral notes. The dry-hopped character is believed to be due to hop ketones and esters (Meilgaard & Peppard, 1986). Sulfur compounds in hops can give sulfury aromas—for example, cheesy or cooked cabbage aromas—to beer. Some of these arise from the use of sulfur sprays on the hops (Hough *et al.*, 1982; Meilgaard & Peppard, 1986).

Raw Materials in the Flavor of Gin, Vodka, and Whisky

The carbohydrate source, whether potatoes, grain, maize, grapes, or molasses, has no effect on the flavor of a very high proof distillate such as vodka. All raw materials serve simply as a source of fermentable sugar. If starch rather than simple sugars is present in the raw material used, then the starch must be broken down to fermentable sugars.

Gin and whisky are both derived from the distillation of fermented grain and thus are made

from similar raw materials. They are in essence distilled, unhopped beer. Gin is produced by distilling this "beer," made mostly from grain, with a smaller proportion of malted barley. Because gin is produced from nearly neutral spirit, most of the flavor derives from ingredients added to the second distillation, or directly to the distillate in American gin. These flavor additives always include juniper berries and usually cardamon seeds as well as other botanicals, which may include dried lemon and orange peel, angelica and orris roots, caraway seeds, anise seeds, fennel (licorice root), and other spices (Chapter 13; Clutton, 1979; Grossman, 1977). The aromas imparted to gin by the use of these botanicals are due to terpenic compounds. Juniper berries contribute α-pinene, γ-muurolene, myrcene, α-terpineol, and other terpenes with pinelike aromas. Coriander, which adds a spicy aroma, contributes primarily linalool, as well as small amounts of α-pinene and other terpenes (Clutton, 1979). The compound D-limonene may arise from the inclusion of citrus peel, and cinnamic aldehyde from the inclusion of cinnamon bark (Simpson, 1977).

Malt whisky is unhopped, distilled beer aged in charred oak barrels. The beer used differs from commercial beer in that there is no pasteurization and no wort boil. Whiskies made from malt beers are termed malt whiskies, and those made from grain beers are termed grain whiskies. The flavor in most whiskies, which are blends of these two types, comes from malt whisky, since grain whisky is fairly neutral in flavor (Watson, 1983).

Kilning of malt is the main flavor-altering process in production of beer for malt whisky (Paterson & Piggott, 1989). Malt aroma compounds are produced by Maillard reactions, as previously described for beer (Watson, 1983), while peating produces pyridines and thiazoles (Paterson & Piggott, 1989), as well as the "smoky" compounds, phenol, cresols, and guaiacols (Howie & Swan, 1984). Pyridine constituents contribute nutty, green, earthy, caramel, roasted, and rubbery aromas (Maarse & Van den Berg, 1994). Since pyridines and thiazoles have lower thresholds than phenols and are recovered to a greater extent in distillation, they may be more important in whisky flavor (Paterson & Piggott, 1989).

Other Raw Materials: Fruits in Wine and Brandies

Fruit brandies have more volatiles than other spirits and in general do not contain flavor impact compounds. Fermentation completely changes the aroma of fruit juice, due to both production of yeast volatiles and metabolism of original fruit volatiles. Methanol, found in all fruit brandies except grapes, is derived from esterase activity on pectin and can contribute a sharp off-flavor (Dürr & Tanner, 1983).

Calvados (apple brandy) flavor is mostly derived from oak aging. Apple and most pear distillates have little aroma. Very ripe Williams or Bartlett pears have esters of *trans*-2-*cis*-4-decadienoic acid (Postel & Adam, 1989), which confer a pearlike aroma on the distillate. Other pears do not produce distillates with varietal specificity, but all have large amounts of 1-butanol and 1-hexanol formed during fermentation by hydrolysis of the corresponding acetates (Dürr & Tanner, 1983).

Stone fruit spirits have higher levels of benzaldehyde and benzylalcohol, ethyl benzoate, and benzyl acetate than other distillates. Benzaldehyde and benzyl alcohol arise from hydrolysis of amygdalin in stones and are present in brandy in much higher concentrations if the mash is fermented with the stones. Kirsch has a high concentration of acetate esters, which are produced from acetic acid formed before fermentation. The main aroma compounds are ethyl acetate, esters of aliphatic acids, benzaldehyde, and benzyl alcohol. Apricot brandy is higher in linalool oxides, terpene alcohols, and γ-lactones than are other stone fruit brandies (ter Heide, 1986).

In fermented apple ciders, specific flavor-active dioxanes (such as 2-methyl-4-pentyl-1,3-dioxane) are generated from the condensation of 1,3-diols, which are unique to the fruit and

acetaldehyde that is formed during the course of fermentation (Chapter 4; Dietrich *et al.*, 1997).

FERMENTATION

Yeast and fermentation conditions are claimed by some to be the most important factors influencing the flavors in alcoholic beverages (Maarse & Van den Berg, 1994; Suomalainen & Lehtonen, 1980). During the primary or alcoholic fermentation of sugar, yeast (most frequently *Saccharomyces cerevisiae*) produces ethanol, carbon dioxide, and a number of by-products, of which alcohols, acetates, and C_4–C_8 fatty acid ethyl esters are found in the highest concentration in wine and distilled beverages (Nykänen & Suomalainen, 1983; Schreier, 1979). Different wine varieties have very similar gas chromatography headspace profiles, all of which are dominated by esters, fusel alcohols, and 2-phenylethanol and its acetate (Noble *et al.*, 1980). Gas chromatography traces of volatiles of whisky, cognac, and rum look very similar. Although some differences are seen in the quantities, the same compounds are present in all distilled beverages (isoamyl alcohol and ethyl caprylate, caprate, laurate, myristate, palmitate, and palmitoleate) (Suomalainen & Lehtonen, 1979).

Yeast Strain

Esters produced by yeast during the primary fermentation contribute to the typical fruity aroma or "fermentation bouquet" that is common to all young wines. Due to rapid ester hydrolysis in the acid wine media, however, differences in the fruity aromas of wines produced by different strains or species of yeast may not be detectable after a short time. After 1 month of storage, there no longer were detectable differences among wines produced with different strains of *S. cerevisiae* and *Saccharomyces bayanus* (Bisson *et al.*, 1990). Only the concentrations of esters differed among wines fermented with four *S. cerevisiae* strains, with one strain yielding higher levels than the rest (Mateo *et al.*, 1992). Differences in the concentrations of volatiles produced by several strains of *S. cerevisiae* and *S. bayanus* have been shown in several investigations, but no accompanying sensory evaluation of the wines has been reported (Antonelli *et al.*, 1999; Falque & Fernandez, 1999). No differences were detected in wine aroma or in levels of terpenols hydrolyzed by yeast glycosidases during fermentation using three different strains of *S. cerevisiae* (Delcroix *et al.*, 1994).

Although different yeast strains can produce wines with significant differences in aroma, they do not produce very distinctively different flavor notes in wine, except in nutrient-deficient musts. In nutrient-limiting situations, the yeast strain may influence the tendency for the fermentation to stick (not ferment all sugar) or to produce hydrogen sulfide. Yeast strains with a genetically determined variation in hydrogen sulfide production have been reported (Romano, 1990; Romano *et al.*, 1988). In wines, *S. cerevisiase* or *S. bayanus* yeast strains are usually selected for fermentation characteristics such as alcohol or cold tolerance rather than flavor. Contradicting this, Romano and colleagues (1998) proposed that specific yeast strains for each type of wines should be chosen based on volatile production as well as viability and sulfur dioxide resistance, since "yeast strains, produce different levels of secondary metabolites."

Inoculations of *S. cerevisiae* and addition of sulfur dioxide are usually made to prevent growth of wild yeasts such as *Hansenula* or *Pichia*, which produce high levels of ethyl acetate (Nykänen, 1986), or of *Brettanomyces*, which yields high levels of ethylphenols; these result in phenolic, horsey, animal, or leather descriptions (Chatonnet *et al.*, 1992a). In white wines (and beers) some *S. cerevisiae* strains can also decarboxylate cinnamic acid derivatives to vinyl phenols, which results in phenolic, smoky, or medicinal off-flavors. One of the enzymes involved in the reaction is inhibited by flavonoid phenols; hence, phenolic odors in red wines do not arise by the same pathway (Chatonnet *et al.*,

1993). Ethyl cinnamate ("cinnamic," "cherry stone" odor), which may arise from yeast esterification of cinnamic acid, was shown to be an important contributor to aroma of Pinot noirs from Burgundy (Moio & Etievant, 1995). In the same study, for the first time ethyl dihydrocinnamate (balsamic aroma) and ethyl anthranilate (fruity odor) were also identified in wine.

In table wines, fusel alcohols have high thresholds and thus contribute little to aroma. In contrast, fusel alcohols are important to the aromas of distilled beverages. Whisky and brandy owe their sensory character in part to fusel alcohols, which have been said to impart a sense of body or depth. A light-bodied brandy has about 0.60–0.75 g/l fusel alcohols at 100 proof, medium-bodied has 0.75–0.90 g/l, and heavy or full has 0.90–1.00 g/l (Guymon, 1972). Acetaldehyde, which accounts for 90 % of the total aldehydes of wine, arises as an intermediate in fusel oil formation. Acetaldehyde synthesis is strain dependent and also occurs at higher concentrations in nutrient-deficient media (Nykänen, 1986).

Unlike with wine, yeast strain is regarded as having a very large effect on beer flavor (Meilgaard & Peppard, 1986). Species differences in ester and fatty acid production have been shown. "Caprylic" flavor corresponds to levels of octanoic and decanoic acids, which vary; lager yeasts (*Saccharomyces carlsbergensis*) produce more than ale yeasts (*S. cerevisiae*). Different yeast strains and species are reported to vary as much as fivefold in the levels of higher alcohols they produce in beer (Engan, 1981). Fusel alcohols are higher in ales, which are fermented at 20 °C, than in lagers, which are fermented at 0 °C. Except for lambic beer, *Brettanomyces* yeast is perceived to be undesirable in beers due to the production of off-flavors (Gilliland, 1981; Guinard, 1990).

Temperature

Higher temperature of fermentation (and higher amino acid levels) favor fusel oil formation in beer and other grain fermentations (Engan, 1981; Nykänen, 1986). Fermentation of wines at higher temperatures produces higher amounts of esters but results in loss by entrainment of the fruity shorter-chain esters (Killian & Ough, 1979) and volatiles, such as the terpenes in the aromatic varieties.

Oxygen Effect

Aerobic fermentations produce a different spectrum of esters than anaerobic fermentations. Generally, more esters are produced when the fermentation is anaerobic. For example, twice as much ethyl hexanoate, ethyl octanoate (both fruity aromas), and phenylethyl acetate (rose, honey aroma) are found in anaerobic fermentations (Nykänen, 1986). Exposure of fermenting wine to air can result in production of acetic acid (from *Acetobacter* infections), acetaldehyde, and greater browning of the nonflavonoid phenolics.

Barrel Fermentation

Wines fermented in barrels are higher in higher alcohols and lower in fatty acid esters (Chatonnet *et al.*, 1991), which results in a somewhat less fruity character in wine. The presence of oak wood during fermentation causes some wood-derived flavor components to be transformed by yeast. Furan aldehydes, many of which have the aroma of grilled almonds, are reduced by yeast during barrel fermentation, which results in furfuryl alcohols. These reduction reactions occur much less when wines are placed in barrels after fermentation. Yeast metabolizes vanillin when wines are barrel-fermented, which reduces the vanilla aroma of barrel-fermented wines (Chatonnet *et al.*, 1991).

Malo-lactic Fermentation

Secondary (malo-lactic) fermentation (MLF) by *Lactobacillus* or *Leuconostoc* bacteria produces volatiles, including the "buttery" component diacetyl (Bertrand *et al.*, 1984).

Acidity is reduced as well through the conversion of malic acid (a dicarboxylic acid) to the monocarboxylic lactic acid. Most red wines undergo MLF and have a detectable buttery aroma, while sourness is reduced. MLF is encour-

aged in Burgundian whites and Chardonnay wines made elsewhere in the world for stylistic reasons. Similarly, MLF is prevented in most aromatic white varieties. Diacetyl and 2,3-pentanedione are also formed in fermentation by yeast (Martineau & Henick-Kling, 1995; Suomalainen & Lehtonen, 1979) and generally are considered to be a defect in beers (Meilgaard & Peppard, 1986).

Lees Contact (Sur lies)

Holding the wines in contact with the yeast lees (*sur lies*) for an extended time after fermentation can alter wine flavor further from that of the starting grape, presumably through the process of yeast autolysis. Chardonnay wines aged on the lees in both stainless steel and oak were less buttery and more toasty than those with no lees contact; effects on fruitiness were inconsistent (LaFollette, 1990). Similarly, characteristic toasty, soy, and caramel flavors arise in sparkling wines aged on the lees of the secondary yeast fermentation. Consistent with this, sparkling wines disgorged after 18 months on the lees were higher in vanilla/butter aroma than the Chardonnay and Pinot blanc base wines from which they had been made (de la Presa Owens *et al.*, 1998). None of the impact volatiles from yeast autolysis have been identified, although an increase in ethyl lactate and diethyl succinate were reported in storage on yeast lees up to 18 months (Postel & Ziegler, 1991). An increase in nitrogen compounds is produced through the activity of proteolytic enzymes, which reach a maximum after up to 5 years on the lees (LeRoy *et al.*, 1990). In contrast, inclusion of yeast lees in Scotch whisky distillation increases the amount of fatty acid esters, such as ethyl caprylate, caprate, and laurate, and of isoamyl acetate in the distillate (Simpson, 1968).

Sulfur Compounds

In wine or beer, sulfides and mercaptans are most often associated with spoilage odors. Hydrogen sulfide is produced as a reactant in the process of fermentation. The level of hydrogen sulfide produced is usually correlated with the rate of fermentation, although none may remain upon completion of fermentation. Factors affecting production of hydrogen sulfide include presence of elemental sulfur (Rankine, 1963; Schutz & Kunkee, 1977), pantothenate deficiency (Wainwright, 1970), high threonine (Wainwright et al., 1972), yeast strain (Eschenbruch, 1978), and possibly low free amino nitrogen (Vos & Gray, 1979). In a survey of wines submitted for analysis of off-odors, DMS (asparagus aroma), ethanethiol (onion, garlic aroma), diethyl disulfide (DEDS; rubber aroma), and less frequently methanethiol (onion, garlic notes) were most frequently detected (Park *et al.*, 1994). In a study of changes in sulfur volatiles during fermentation and storage, dimethyldisulfide (DMDS; rubber aroma), diethyl sulfide (DES; rubber odor), and methanethiol were consistently present at higher than threshold levels, which suggests that they played a major role in the "reduced" odor of the spoiled wines (Chatonnet *et al.*, 1992b). Hydrogen sulfide, DMS, sulfur dioxide, methanethiol, ethanethiol, DES, and DEDS have been found in beer. Distilled spirits often contain DMS, DMDS, carbon disulfide, methanethiol, and hydrogen sulfide (Suomalainen & Lehtonen, 1979). DMS, DMDS, dimethyl trisulfide, and 2-methyl-2-(methyl dithio) furan are considered to be important compounds in whisky aroma (Philp, 1986). In contrast to these sulfur volatiles associated with spoilage, two mercaptans (2-mercaptoethyl acetate and 3-mercaptopropyl acetate) were identified in Sauvignon blanc that have toasted, roasted meat aromas (LaVigne-Cruége *et al.*, 1998).

DISTILLATION

The sensory character of alcoholic beverages is changed as the absolute and relative amounts of volatiles are altered by distillation. In addition, the partition coefficients of volatiles vary considerably with ethanol concentration, which further alters the headspace volatile composition from the starting wine or wort. Nonvolatiles, including polyphenols or organic acids, are virtually eliminated by distillation. The composi-

tion of distillate is determined by many factors, including still type, the degree of rectification, and the selection of fractions taken for inclusion in the distilled beverage.

Vodka, like gin, is produced from neutral or near-neutral spirit rectified to very high proof using continuous stills. Since vodka is not normally flavored by additives, it has little sensory characteristics other than the sensation of ethanol. To ensure that vodka has no aroma, it is often treated with activated charcoal. The only congeners found in vodka are a trace of propanol and ethyl acetate (Clutton, 1979).

Customarily, the most volatile cut (heads) is omitted from the fractions collected for distilled beverages. The heads fraction contains several aroma compounds usually considered to have negative sensory impact, including acetaldehyde, sulfur dioxide, and ethyl acetate (Guymon, 1974). Although the aldehyde content is reduced by the omission of heads, it usually increases during maturation in beverages that are oak aged (Nykänen, 1986).

Fusel oils are the most abundant congeners of distilled beverages and tend to distill toward the middle of a continuous column, peaking at about 130 proof. A distillate such as vodka collected at very high proof will have lower concentration of fusel oils and all other odorous volatiles than a brandy taken at 170 proof unless special techniques on a continuous still are used (Guymon, 1972, 1974).

Fatty acids and their ethyl esters comprise the second most abundant group of congeners in distilled beverages and distill in a pattern similar to that of fusel oils. Some of the more volatile ethyl esters are lost in the heads fraction of pot distillations. The major esters, such as the ethyl, isobutyl, and isoamyl esters of short-chain fatty acids, have fruity aromas. Higher boiling esters, such as the ethyl esters of caprylic and capric acids, often predominate (Guymon, 1974). High-boiling esters such as ethyl esters of myristic, palmitic, and palmitoleic acids (this last one mainly in Scotch whisky) are also found (Suomalainen & Lehtonen, 1979). Caproic, caprylic, and capric acids, which have goaty to soapy aromas, tend to be concentrated in the fraction usually discarded (tails) (Guymon, 1974) and thus are usually present at lower concentrations in distillates.

Thermally Induced Chemical Reactions

Distillation alters flavor not only due to its effect on the relative proportions of compounds but also due to chemical reactions that take place during the heated conditions of distillation. Maillard reactions can form heterocyclic compounds during distillation (de Rijke & ter Heide, 1983), particularly in direct-fired pot stills, where furfural may be formed (Simpson, 1971). Sulfur-containing pyrolysis products formed during distillation, such as thiophenes and polysulfides, play an important role in the flavor of whisky, adding a heavy roasted character (Maarse & Van den Berg, 1994).

Acids and alcohols react to form esters, and many reactions occur in the hot vapor phase, such as the reduction of aldehydes to acids and alcohols (Watson, 1983). Acetals form in distillation due to the acid-catalyzed addition of two alcohols to an aldehyde. During distillation diethyl acetal is formed at concentrations well above its aroma threshold (Nykänen & Nykänen, 1983), imparting a "delicate fragrance" to distilled beverages (Swan, 1993). Coumaric and ferulic acids derived from barley or grapes can break down to compounds with spicy or medicinal aromas, such as 4-vinylguaiacol, due to the heat of distillation (Paterson & Piggott, 1989).

The fruity or flowery aromas of brandy, which are due largely to terpenes, are altered during distillation. Glycosylated terpenes are hydrolyzed in the hot acidic conditions of the brandy still, which results in a higher concentration of free terpenes, and thus intensification of aroma, in the distillate (Strauss & Williams, 1983). Thermally induced reactions result in further modification of terpenes, including the decomposition of odorless terpene polyols to terpenes with low aroma thresholds.

The pungent, peppery aroma in new spirits, whisky, cognac, or rum is believed to be due to acrolein, a glycerol derivative that can form during the heat of distillation from a precursor pro-

duced by bacteria during fermentation (Lyons 1974; Nykänen, 1986).

Still Type

The still type and technique affect the flavor of brandy and whisky. Many reactions catalyzed by the copper stills and condensers occur during distillation (Watson, 1983). Scotch whisky, malt whisky, and cognac are produced using two batch distillations in small copper pot stills. Armagnac brandy is produced in one batch distillation, while rum and vodka are usually produced in continuous stills. Fractions taken at high proof from a continuous still differ from the product collected from the batch distillations. Higher congener concentrations and heavier flavors are promoted by the use of pot stills, which do not fractionate volatiles as effectively as do continuous stills. Fusel oil concentrations are high in pot-distilled malt whisky and brandy, whereas column-distilled gin, vodka, and grain whisky have lower levels (Hough *et al.*, 1982). The rose-flavored compound 2-phenethanol is found in brandies produced in pot stills but not in those produced in continuous stills (Simpson, 1971). Furfural is formed in direct-fired pot stills but does not arise during distillation in continuous stills (Simpson, 1971). Dutch gins, which are pot-distilled at approximately 50 % ethanol in both distillations, maintain the flavor of malt due to the low proof at which they are distilled, which allows more aroma compounds to be retained in the distillate. In contrast, the lighter-flavored English and American gins are distilled at higher proofs, 90–94 % in the first distillation (Grossman, 1977).

CONTRIBUTION OF AGING TO FLAVOR

Reactions during Aging

The flavor of most alcoholic beverages immediately after fermentation or distillation only approximates that of the finished product. After the sudden and dramatic changes in composition effected by fermentation and distillation, chemical constituents react slowly during aging to move toward their equilibria, which results in gradual changes in flavor. The complexity of many beverages, including wines, brandies, and whiskies, can be further increased by the oxidation and extraction of oak barrel aging. A less dramatic change, due to slower oxidation without oak extraction, occurs when products such as wine or beer are matured in inert tanks or aged in bottles. Most products eventually decrease in quality, often due to excessive oxidation, when aging in tank, barrel, or bottle is too lengthy.

Vodka and gin do not change in character during aging and so require no period of maturation prior to consumption. After distillation and reduction of proof, they are stored in inert tanks until bottled (Grossman, 1977).

Oxidation

Newly fermented or "green" beer is matured only briefly, under reducing conditions, to improve the aroma. The levels of diacetyl, the buttery aroma of which is considered a defect in beer, and of other aroma compounds decrease during the "diacetyl rest," a brief maturation period used to stabilize beer flavor prior to bottling (Hough *et al.*, 1982). Further aging of beer results in deterioration of flavor due to oxidation, which produces "stale" flavors described as raisin, honey, molasses, caramel, bready, paper/cardboard, or cabbage aromas (Meilgaard & Peppard, 1986) and bitter, astringent, or harsh tastes (Hashimoto, 1981). Oxidative changes result in the production of unsaturated aldehydes, especially 2-trans-nonenal, acetaldehyde, and furfural, which contribute a "cardboard" aroma defect to beer at concentrations below 1 ppb, 20–40 ppm, and 2 ppm, respectively (Hashimoto & Eshima, 1977). Unhopped beer is much less likely to develop oxidized aromas during storage, which implicates the oxidation of hop isohumulones in the development of beer staling (Hashimoto, 1981). Oxidation in bottled beer when headspace volume is high can result in a catty, boxwood, or ribes aroma due to the

presence of 4-mercaptopentan-2-one (Hough *et al.*, 1982), a compound very similar in both aroma and chemical structure to that associated with the cat urine or boxwood aroma in Sauvignon blanc.

Oxidation of small phenols such as flavonoids, cinnamates, and benzoic acid derivatives is reported to increase bitterness and astringency in aging beer (Hashimoto & Eshima, 1977). Extended aging, however, can result in a decrease in bitterness due to the breakdown of iso-α-acids (Meilgaard & Peppard, 1986).

White wines such as Chardonnay may be improved by limited oxidation, but excessive oxidation results in the loss of fruity character and the acquisition of oxidized aromas. Extreme oxidation results in the nutty or acetaldehyde aroma of sherry. The transition between an overoxidized white wine and a minimally oxidized sherry occurs at 60 ml oxygen/l wine (Singleton *et al.*, 1979). Up to this level of oxygen, red wine "improves" through reduction of fruitiness and development of "aged" compounds, adding complexity and "mature" character. The absorption of over 180 ml/l oxygen by red wines results in lack of fruitiness, development of oxidized character, and brown color (Singleton, 1987).

The increased susceptibility of a white wine or beer to noticeable oxidation, relative to other alcoholic beverages, is due largely to the quantity and nature of their phenolic constituents. Phenols form a reservoir of oxidizable substrates in alcoholic beverages, which can increase the amount of oxidation that can occur without negative sensory consequences. White wines, which are much lower in phenols than reds, are particularly subject to oxidation, with its characteristic loss of fruity aroma and development of brown color.

Much oxidation in wines occurs when molecular oxygen and vicinal diphenols react to form quinoidal compounds. The hydrogen peroxide thus formed is a very strong oxidant that easily reacts with other wine components. Due to its very high concentration in wines, ethanol is most frequently oxidized by hydrogen peroxide, forming acetaldehyde (Singleton, 1987; Wildenradt & Singleton, 1974), the chemical cause of oxidized wine aroma. Acetaldehyde levels in beers, wines, brandies, and whiskies commonly increase during aging. Further oxidation of acetaldehyde may result in formation of small amounts of acetic acid.

Oak-aged distilled products that do not contain phenols derived from raw materials, such as brandy and whisky, can undergo similar oxidation reactions catalyzed by vicinal diphenols extracted from oak. Ellagic and gallic acids derived from the hydrolysis of oak ellagitannins can promote the oxidation of ethanol to form acetaldehyde and diethyl acetal (Swan, 1993). In contrast, the ethanol in alcoholic beverages lacking vicinal diphenols derived from raw material or wood aging, such as gin and vodka, does not readily oxidize to acetaldehyde.

Sherries are produced by deliberately allowing slow oxidation of maturing wines, as are other dessert and aperitif wines such as Marsala or Madeira. Flor sherries, produced with the film yeast *Saccharomyces fermentati*, are high in acetaldehyde, whereas sherries made with baking at high temperatures are higher in furfural derivatives (Webb & Noble, 1976).

Esterification and Hydrolysis

Fermentation esters produced by yeast during fermentation at concentrations above their chemical equilibria hydrolyze slowly after fermentation, which results in a loss in fruitiness. Acetate esters of higher alcohols hydrolyze faster than ethyl esters, while longer-chain ethyl esters hydrolyze more rapidly than shorter esters (Ramey & Ough, 1980). Esterification of acids and alcohols also occurs during aging. Tartaric acid and other organic acids slowly esterify with ethanol to reduce acidity and diminish sourness during maturation. The formation of these esters has little affect on aroma (Edwards *et al.*, 1985). Distilled products with higher concentrations of ethanol may undergo more extensive esterification, acetalization, and ether formation in aging (de Rijke & ter Heide, 1983).

Terpene glycosides decrease slightly during fermentation and are further hydrolyzed during subsequent aging. After 6 months of storage,

16 %, 27 %, and 34 %, respectively, of geraniol, linalool, and nerol glycosides in a Muscat of Alexandria wine hydrolyzed due to acid catalysis (Park & Noble, 1993). Conventional storage of white Riesling wines for 40 months resulted in hydrolysis of 60–80 % of the glycosides (Zoecklein *et al.*, 1999). Consequently, the aroma of wines that owe much of their aroma to terpenes, such as Gewurztraminer or Riesling, may increase early in maturation. Generally, over longer periods of storage, the free monoterpenes are interconverted through hydrolysis and oxidation (Williams *et al.*, 1982). This produces a decrease in floral or fruity aromas as the floral terpenes with low thresholds are converted to compounds associated with off-odors, such as α-terpineol, which has a piney note, and to terpene oxides or polyols, which are odorless or have very high thresholds (Simpson, 1979).

During aging of wines, furfural, vitispirane, and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) have been shown to increase (Simpson, 1978). Of these, the only component that contributes significantly to aroma is TDN, which is associated with a kerosene or petrol off-odor in aged Rieslings. Higher levels of TDN are produced in wines from higher maturity grapes (Strauss *et al.*, 1987), in wines from vines with more light exposure (Marais *et al.*, 1992b), and in wines stored at higher temperatures (Marais *et al.*, 1992a). One of the precursors of TDN is a hemiacetal that is thought to be present in grape juice as a glycoside (Winterhalter, 1991).

Evaporation

Aroma and flavor may be concentrated during aging due to evaporation (Blazer, 1991). Evaporation is a function of temperature, air speed, the area of wine exposed to air or inert gas, and the composition of air or gas in contact with liquid surface or barrels. Loss of ethanol and water from barrels occurs slowly as liquid migrates through wood and is dependent on barrel size, stave thickness, and type of wood, as well as the relative humidity in cave or cellar. When relative humidity is maintained at high levels, as occurs in caves or humidity-controlled aging cellars, although less evaporative loss occurs, the level of ethanol decreases since more ethanol is lost than water. Conversely, aging in facilities that do not control humidity generally results in an increase in alcohol content (Blazer, 1991).

Effects of Oak Aging

Aging of alcoholic beverages in oak is usually conducted to develop characteristic flavors, either through extraction of volatile oak compounds in new barrels or through slow oxidative changes in older barrels from which little oak volatiles can be obtained. Fresh distillate usually has a simple, harsh flavor that changes dramatically upon aging in wood, becoming smoothed and mellowed upon aging. During oak aging, flavor is changed through extraction of hydrolyzed or ethanolyzed wood compounds; slow oxidation; evaporation of ethanol, water, and volatile compounds; and chemical reactions leading to the formation of new compounds (Maga, 1989; Mosedale & Puech, 1998). In Scotch whiskies, intensities of "smoothness," and spicy, vanilla, floral, and woody attributes increased upon aging in wood, while phenolic, sour, meat, and catty notes decreased (Piggott *et al.*, 1993). Nonvolatile wood extractives were suggested to affect the headspace concentrations of ethyl esters in brandies and whiskies, which presumably could affect their flavors (Conner *et al.*, 1994; Piggott *et al.*, 1992).

The concentration and composition of aroma volatiles imparted by oak wood to wine and distilled beverages is influenced by many factors, including oak species, source of oak wood, length of time and climate in which oak wood is seasoned, toast or char level of oak, cooperage techniques, and age and size of the barrel, as well as time and temperature of storage in the oak cask (Sefton *et al.*, 1993a; Swan, 1993).

Compounds Extracted from Oak

Directly extractable compounds in oak include vanillin, hydroxymethylfurfural, and ethylmaltol (Swan, 1993), and maltol (Nishimura *et al.*,

1983). Vanillin and syringaldehyde, responsible for most of the vanilla flavor that is characteristic of oak-aged beverages, arise from the oxidation of coniferyl and sinapic alcohols, respectively, which are produced by ethanolysis of oak lignins (Reazin, 1981). Eugenol and other volatile phenolic compounds contribute to the spicy aroma in wines aged in new oak, as illustrated by the fact that Cabernet Sauvignon wines aged 1 year in oak were higher in vanilla, oaky, and spicy aromas than wines aged in glass (Aiken & Noble, 1984). The *cis* isomer of oak lactone (β-methyl-γ-octalactone) has a characteristic oak wood aroma perceptible at very low concentrations in oak-aged alcoholic beverages. One part per million of oak lactone in spirits results in an oaky, slightly coconut aroma (Reazin, 1981). The aroma of oak lactone is modified by furfural to decrease the woody aroma and increase a caramel/vanilla aroma (Reazin, 1981). The concentration of oak lactone varies more with the location in which it was air dried than with country of origin (Sefton *et al.*, 1989b), although the ratio of isomeric forms of oak lactone varies with the source of the wood (Waterhouse & Towey, 1994). Limousin oak has very low levels (Maga, 1989), and American oak has higher levels than French oak (Guymon & Crowell, 1972).

The tannic constituents of oak wood, ellagitannins, hydrolyze during wine or spirit maturation to ellagic and gallic acids. Like the phenolic components of wines, these extracted phenols can serve as oxidation substrates and promote oxidation of other beverage components, as well as contributing to bitterness and astringency. Simple sugars increase in alcoholic beverages aged in oak barrels by extraction or upon acid hydrolysis of hemicellulose (Maga, 1989; Singleton, 1974). Although levels of these sugars are not usually high enough to contribute to the perception of sweetness, they contribute to the formation of furfural and related flavor compounds (Maga, 1989).

Norisoprenoids can also be extracted from oak wood by alcoholic beverages. During maturation these oak-derived norisoprenoids can further degrade to terpenes or other aroma compounds, which leads to the violet-fruity aroma of β-ionone or the tobacco aroma of a norisoprenoid-derived bicyclic ether (Sefton *et al.*, 1989b).

French versus American Oak

The source of oak has a significant effect on the nature and quantity of oak extractives and flavor. American and French oaks, the types most commonly used to age wine or brandy, are derived from different species. French oak used for cooperage is harvested from *Quercus robur* and the similar species *Quercus sessilis*. American oak, which usually is grown in a broad region including Missouri, Kentucky, and Arkansas, is derived from white oak that is *Quercus alba* and several related species (Singleton, 1974). Whisky and Rioja wines are usually aged in American oak, whereas both American and French oak are used for wine aging.

Wines and brandies aged in French and American oak can often be distinguished by experienced tasters (Rous & Alderson, 1983; Singleton, 1974), although they may be indistinguishable after long storage time in barrel, or storage in used barrels. White wine aged in American oak has been distinguished from the same wine aged in French oak primarily due to the higher intensity of "oak" aroma in American oak–aged wine (Jindra & Gallander, 1987). Inconsistent with this report, model wines aged in American oak were perceived to be lower in aroma intensity, particularly in spicy aroma, than those aged in French oak (Francis *et al.*, 1992a). Although new barrels were employed, there was no significant difference in flavor between Cabernet Sauvignon wines aged in French barrels and those aged in American barrels for 3 months to 1 year, which suggests that the effect of oak source can be overridden in strongly flavored wine (Aiken & Noble, 1984). Although European oak imparts more extractable material, phenols, and tannins to ethanolic solutions, American oak is considered to impart more flavor (Singleton, 1974). Oak lactone, furfural, and 5-methyl furfural levels are much higher in American oak than in French oak (Guymon & Crowell, 1972). American and French oaks have

also been found to differ in norisoprenoid and terpene composition (Sefton *et al.*, 1989b).

New versus Used Barrels

More flavor compounds are extracted by wines or spirits from new oak barrels than from used ones. In whisky production, most congeners are extracted by the first barrel fill of a charred whisky barrel (Reazin, 1981). Levels of oak lactone and vanillin are high in new oak barrels, which therefore tend to impart strong oaky and vanilla aroma characters to wines or spirits so aged. New French barrels contribute much higher levels of oak lactone and vanillin to wine than do recycled casks (LeBrun, 1991).

The differences between oaks of different origin such as French and American oaks become less pronounced as barrels age and extraction of flavor compounds is diminished. Although new French oak barrels impart more phenolic extractives to wine than do new American oak barrels, older barrels of both origins have been found to impart comparable levels (Rous & Alderson, 1983).

Barrels that are not new often induce less oxidation and can lead to reductive aromas (Chatonnet *et al.*, 1991). In wines, older barrels may also impart a spicy aroma due to 4-ethyl guaiacol, or a "barnyard" aroma due to 4-ethyl phenol. Both of these ethyl phenols are products of bacterial metabolism that arise in the malo-lactic fermentation and accumulate in barrel wood (LeBrun, 1991).

Cooperage Techniques

The means by which oak staves are dried (air drying or seasoning versus kiln drying) has a more significant effect on wine aroma than the methods used to bend staves (steam versus fire heating) (Pontallier *et al.*, 1982). The climate and humidity in which seasoning occurs affects oak-derived flavor. Vanillin and oak lactone levels were higher when the same oak was seasoned in a hot, dry location than when it was seasoned in cooler, moister regions (Francis *et al.*, 1992b; Sefton *et al.*, 1989b). Air-dried oak has been found to be higher in oxidizable lignin, vanilla, ellagitannins, and ellagic acid, and lower in hydroxymethylfurfural, than kiln-dried oak.

Seasoning or weathering oak, a practice often considered to leach undesirable tannins, can increase or decrease the concentrations of oak flavor compounds (Swan, 1993). Cedar and nutty aromas were higher, and raisin aroma was lower, in model wine extracts stored in seasoned wood than in those stored in nonseasoned wood (Francis *et al.*, 1992b).

Barrels made by bending staves over open flame are often toasted or charred, contributing toasted, smoky odors on aging. Toasted oak has dramatically higher levels of these vanillin and furfural derivatives. In addition to cyclotene and maltol, 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran, furaneol, and dihydromaltol actively contribute to the "toasty caramel" aroma of heated oak (Cutzach *et al.*, 1997). The characteristic aroma and body of American whisky is due almost entirely to charred oak extractives. Lignin and hemicellulose break down thermally during oak charring, which results in higher levels of aromatic aldehydes, tannins, and sugars than in uncharred barrels (Reazin, 1981). Heating and charring have been found to increase the amount of small phenolic aldehydes and extractable lignin, as well as of furfurals and other thermally induced flavor chemicals such as furans, pyrazines, pyridines, and pyrans (Clyne *et al.*, 1993; Maga, 1989).

Aging whisky in charred barrels increases the intensity of aromas associated with older spirits, such as smooth, vanilla, and sweet, while decreasing those associated with younger products (pungent, sour, oily) (Clyne *et al.*, 1993). Whisky barrels can be recharred to increase congener extraction, but recharred barrels impart no more than one-half the level of congeners imparted by new charred barrels (Reazin, 1981).

CONCLUSION

Over 1,300 volatile compounds have been identified in alcoholic beverages (Nykänen, 1986). Although odor thresholds and aroma

descriptions have been published for many of these compounds, the flavor of complex systems, such as beer, wine, or whisky, cannot be predicted from this information alone. The major products of yeast fermentation, esters and alcohols, contribute a generic background flavor to all fermented beverages. Except in the few instances in which impact compounds have been identified, it is subtle combinations of trace components that usually elicit the characteristic aromas of these complex beverages.

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