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Relevant Websites

http://www.enonline.sh.cn – Shanghai online.

http://www.sytu.edu.cn – A site of the Southern Yangtze University in China. Contains an English translation of a wide-ranging survey of alcoholic drinks and beverages in China from an historical viewpoint to the technology used as well as aspects of the legal and regulatory side of the industry.

http://www.foodreference.com – A site dealing in general with all aspects of food. It includes daily food and beverage news, a culinary quiz and a "Today in food history" section. There is a wealth of information. Use of search function to search for "rice wine."

http://www.internationalrecipesonline.com – Recipes for using rice wine are available on the site using the search function.

Distilled

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Introduction

Distilled beverages that are sold commercially are produced from plant materials (Table 1) and their

Table 1 Raw materials used for the production of some major distilled beverages

Products	*Raw materials*
1. Scotch malt whiskies[a]	100% malted barley
2. Scotch grain whiskies[a]	Wheat or maize (+ malted barley)
3. Cachaça	Sugar cane juice only. Unlike "industrial" Cachaça, which is made from cane products (e.g., molasses) and sugar, only fresh sugar cane juice is used to produce traditional, "artesanal" Cachaça
4. Rum	Molasses mainly and sugar cane juice
5. Irish whiskies	100% malted barley
	Barley + malted barley
	Maize + malted barley or enzymes
6. Gin	Maize or wheat (with malted barley or enzymes for starch conversion into sugars). Pot still distillation of Juniper berries and other botanicals or, addition of spirit to Juniper berries and botanicals or to the essence of these plants
7. Tequila (100%)	Agave (*Agave tequilana* Weber Var. Azul) plant
Tequila	Agave plant + sugar or syrup
8. Vodka	Cereals, grape juice, raisins, molasses, potatoes (with or without enzymes for starch conversion)
9. American whiskies (bourbon, corn, rye, Tennessee)	Maize + rye (with malted barley: plus or minus commercial hydrolytic enzymes)
10. Canadian whiskey	Maize, rye, and malted barley and malted rye + amylolytic and glucanolytic enzymes
11. Brandy	
Cognac	Grapes
Armagnac	Grapes
Eau de vie	e.g., pears, raspberries, cherries, and plums
12. Aquavit	Grain or potato (with malted barley or enzymes for starch conversion). Neutral spirit from grain or potato is then redistilled with flavorings. Caraway is the main flavoring and citrus peel. Cardamom and anise can be incorporated as well

[a] Japan also produces malt and blended whiskies.

Table 2 Types of stills used in production of distilled spirit beverages

Products	*Stills*
1. Scotch malt whisky	Usually, two large copper pot stills (wash and spirit) – tube condensers
2. Scotch grain whisky	Continuous (patent) still (analyzer, rectifier)
3. Cachaça	Small copper pot stills with worm condenser coils. Traditional (e.g., "artesanal") Cachaça is produced using pot stills. Single distillation like Aramagnac. Continuous stills used to produce "industrial" Cachaça
4. Rum	Continuous still (Analyzer, rectifier) – Puerto Rican (light rum). Distillation in series of two or three copper pot stills (to avoid double distillation in one still). Cooling coil condensers present: Jamaican (high flavor (heavy) rum)
5. Irish whiskey	Three copper pot stills (viz: wash, low wine, and spirit). Triple distillation
6. Gin	Continuous still (analyzer, rectifier) then copper pot stills for distillation with botanicals
7. Tequila	Copper pot still (double distillation) or Continuous still (analyzer, rectifier)
8. Vodka	Continuous still (analyzer, rectifier)
9. American whiskey	Continuous stills or continuous still plus doubler for additional distillation
10. Canadian whiskey	Continuous still with analyzer column, extraction column, and rectifying column. Pot stills
11. Brandies	
Cognac	Small copper pot still with cooling worm, direct fired instead of internal heating coil. Double distillation
Armagnac	Small copper pot still or small single column continuous still. Single distillation in pot stills, like traditional Cachaça
Eau de vie	Copper pot still – double distillation (analyzer, rectifier)
12. Aquavit	Continuous still (analyzer, rectifier)

distillation processes (Table 2) are clearly defined. Each product has distinct aromas and flavors which reflect raw materials, distillation process, and post-distillation treatments such as maturation in wooden (e.g., oak) casks. The flavor compounds in distilled beverages are referred to as congeners. Different beverages can have small differences in congener levels but have large differences in flavor and aroma intensities. Flavor and aroma intensities may also relate to the complex modulating effects, which different congeners have on each other, and to the physiological and cultural differences of consumers. In distilled spirit beverages, ethanol is the main compound as regards quantity and the congeners can be regarded as "ancillary products" of the natural production of ethanol.

Ethanol of distilled beverages is produced from the different sugars derived from the raw materials used. The mechanisms of production of congeners are very complex. Some are produced by yeast during fermentation, others are produced during distillation, and some develop during maturation. In some distilled beverages such as gin, flavor materials are added. The term "distilled portable spirits" relate to distilled products that are eventually packaged and sold as beverages for human consumption (Tables 1 and 2). The production procedures of many distilled beverages are defined by law. For example, Scotch whisky means whisky distilled and matured in Scotland and Irish whiskey means whiskey distilled and matured in Ireland. Scotch malt whisky is made from malted barley. The blended brands of Scotch whiskies are blends of Scotch malt whiskies and Scotch grain whiskies. Scotch malt whiskies are produced in pot stills and Scotch grain whiskies are produced in continuous patent stills. Only enzymes from malted barley can be used in Scotch whisky production. In the United States, bourbon whiskey must be produced, from a mash conversion of not less than 51% corn grain and rye whiskey must be produced from not less than 51% rye grain respectively. Cognac or tequila can only be made in respective areas of France or Mexico. In many countries, a minimum age of post-distillation maturation in wooden barrels is designated by law. Also, in this regard, Scotch whisky can only be matured in Scotland in oak barrels and bourbon can only be matured in "new" (charred) oak barrels in the United States of America.

Historical Background

The exact dates of development of many distilled beverages are not known. The Chinese may have developed the distillation process in ancient time. The ancient Egyptians had alembics which could have produced alcoholic drinks but it was the Moors who were responsible for distributing the technique and for the derivation of the word "alcohol" which is derived from the old Arabic word "Al-Kuhl." The distillation process is therefore an ancient-world technology and is known to produce a concentrated alcoholic essence of the initial ferment, which contained lower levels of ethanol. A sugar solution of ~14–16% will, after fermentation by yeast, yield ~7–8% ethanol. According to Gay-Lussac, 100 lbs of glucose should, after fermentation by yeast in ideal conditions, yield 48.89 lbs of carbon dioxide and 51.11 lbs of ethanol. But, according to Pasteur, only ~95% of these products can be expected in fermentation systems. Ethanol is a simple alcohol. It is a member of a large group of alcohols, some simple, others complex, but all containing carbon, hydrogen and oxygen, and hydroxyl groups, which have replaced hydrogen atoms.

Although it has been suggested that the Crusaders brought the technique of distillation to Europe in the eleventh to twelfth centuries, it was not long after this period that distillation activity was discovered in Ireland. The first written record of Scotch malt whisky appeared in 1494. The word whisky is spelt "whisky," when applied to Scotch but is spelt "whiskey" when applied to Irish, Canadian, and American whiskies. In 1931, the Coffey (continuous or patent) still was invented by Aeneas Coffey to produce Scotch grain whisky in large quantities. The first blended Scotch whiskies (i.e., mixtures of malt and grain whiskies) were produced by Andrew Usher in 1860. Blended whiskies are now ~93% of the Scotch whisky market worldwide.

Although the production of vodka, in Russia, dates back to the twelfth century, significant development of other major spirit beverages such as tequila (Mexico), Cachaça (Brazil), and cognac (France) took place in the sixteenth century. A large rum industry, operated by slaves in the West Indies, was very productive in the seventeenth century. Gin was being produced in Holland in the seventeenth and eighteenth centuries. By 1743, the annual consumption of gin in Britain was 70 million liters (Ml) for a population of 6 million people. The devastating effect of excessive drinking of gin was portrayed in Hogarth's (1697–1764) famous etchings of gin drinkers. American whiskies developed in the eighteenth century and Canadian whiskey appeared in the nineteenth century. Canadian rye whiskey came to prominence in the 1940s. Examples of other localized, smaller-volume products of the distilled spirit market are: aquavit (Denmark), arrack (e.g., Turkey), grappa (Italy), marc (France), okolehao (Hawaii), ouzo (Greece), pisco (South America, e.g., Chile and Peru), mao tai (China), and mezcal (with or without "worm" (Mexico)).

As regards the science and technology of distillation, the first study of the distilling process, where a liquid containing many compounds is vaporized, separated, and collected as desirable (drinkable) was made by the French alchemist Arnold de Villeneuve in 1310. Taxation of distilled spirits is an important source of revenue for many producing countries. For example, the first taxation on Scotch whisky was in 1644 at ~40 pence per gallon. That taxation persists today at the impressive figure of about £88 per gallon for pure alcohol. Of all the spirits in the world, vodka sells in the largest volume. Bacardi rum is the largest brand. Scotch whisky earns the largest income of the brown spirits and Cachaça is the spirit product that is consumed in the largest volume in one country (Brazil). It is produced in the largest number of production facilities (*c.* 18 000).

Malting and Mashing Processes

Malting

Scotch malt whisky is produced from malted barley of known varieties. Malted barley is derived from the malting process (Figure 1). In this process, ~25–500 t of barley are steeped in water and air-rested for ~48 h at ~16°C. The water is drained and the grains allowed to germinate (grow) for a period of ~5 days at 16–18°C. The germinated grains are then kilned (dried) at 60–70°C. During kilning, peat may be burnt to "peat" the malt because the

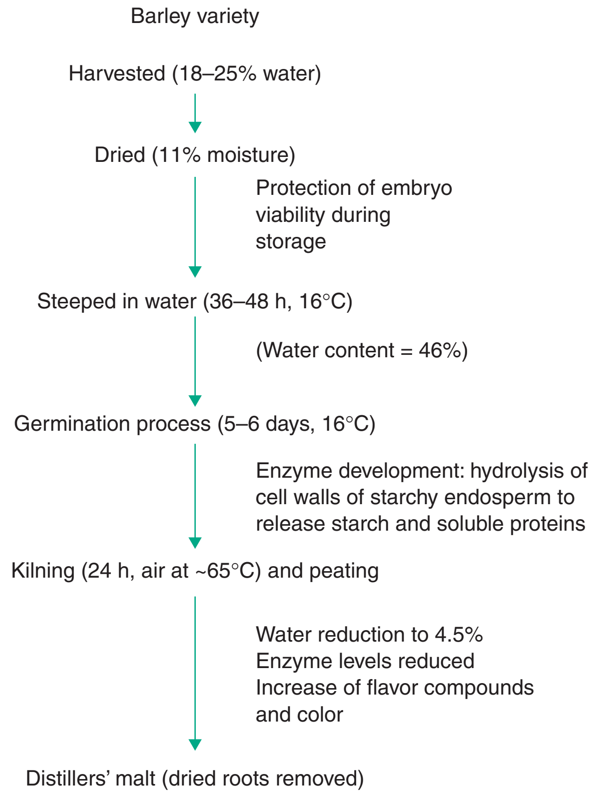

Figure 1 Production of the distillers' malt.

smokey-peaty (phenol: 0–50 ppm) flavor of malted barley is an important flavor note of many brands of Scotch whiskies.

During the germination process, the plant hormone gibberellic acid is produced in the growing embryo. This natural hormone is transported to the aleurone (bran) layer which encloses the starchy endosperm (Figure 2). The aleurone is induced by the hormone to synthesize endosperm-degrading enzymes such as cell-wall-degrading endo-β-glucanases; storage-protein-degrading proteases and starch-degrading α-amylases. Other enzymes such as β-amylase (maltose producing) and carboxypeptidases (amino acid producing) develop in the starchy endosperm. Together, these enzymes modify (disrupt) the starchy endosperm so that subsequent milling and extraction (mashing) of the malt in hot water can occur readily. During this process, starch is converted into fermentable sugars, amino acids are extracted and produced. Vitamins and minerals are also extracted. These substrates are required, by growing yeast cells during fermentation, to produce ethanol and flavor compounds (Figure 4).

Distillers set laboratory specifications as regards the quality of the malt they require to produce their whisky products. For example, such malts must have a high fermentable extract potential of ~68% and fermentability potential of ~87%, amino acids (free amino nitrogen) should be 130–140 ppm and the modification of the malt, assessed in terms of friability should be at least 90% to enable easy milling and extraction.

Nitrosamines and ethyl carbamate are natural carcinogenic compounds, which develop during the kilning and distilling processes respectively. Very low levels of nitrosamines are specified (none or 1 ppb max.). Glycosidic nitrile is also specified at very low levels (3.0 g t^{-1} of malt) because it is the precursor of ethyl carbamate. Only malted barley can be used to produce Scotch malt whisky. In Scotch malt or grain whisky production, all the enzymes required to convert the starch and proteins to sugars and amino acids must be derived from the malt. By law, no extraneous enzymes can be added.

The Mashing Process – The Starch Degradation and Sugar Extraction Process

Cereal grains (Tables 1 and 3) used in whisky (whiskey) production contain significant quantities of starch and cell wall polysaccharides such as β-D-glucans and pentosans.

Cooking solubilizes both the large (10–30 µm) and small (< 5 µm) starch granules (Figure 3). Heating of raw starch granules beyond their gelatinization temperatures is necessary before they can be converted optimally into sugars by amylolytic enzymes. The large starch granules of wheat, barley, and rye, gelatinize between 63°C and 65°C. The gelatinization temperature of rye starches can extend to 70°C. Small starch granules will gelatinize at ~80°C. Maize and sorghum starches (10 µm) gelatinize above 70°C, and are usually cooked. Malt also contains starches which must be gelatinized to realize the extract that malt can contribute to the mash. Therefore, when

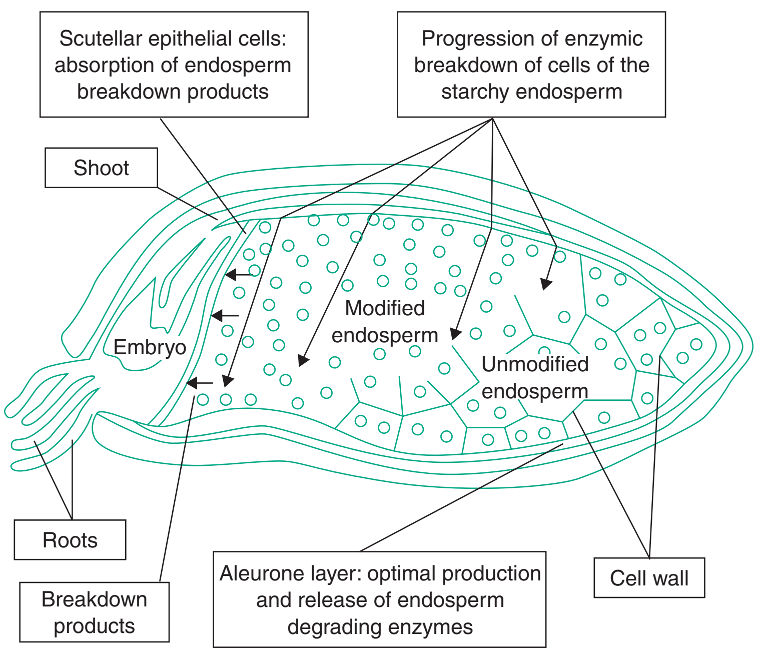

Figure 2 Progression of endosperm breakdown by endosperm-degrading enzymes during the malting process (×34).

Table 3 Constituents of some cereals (%)

Cereals	*Starch*	*Gelatinization temperature (°C)*	*Protein*	*Lipid*	*β-D-glucan*	*Pentosan*
Barley	65	63	10.0	3.0	3.5	9.0
Wheat	64	60	11.0	3.0	0.5	8.5
Rye	60	65–70	13.0	2.5	1.5	9.0
Maize	70	>70	11.0	5.0	0.3	3.5
Sorghum	70	>70	10.0	3.0	0.3	3.0

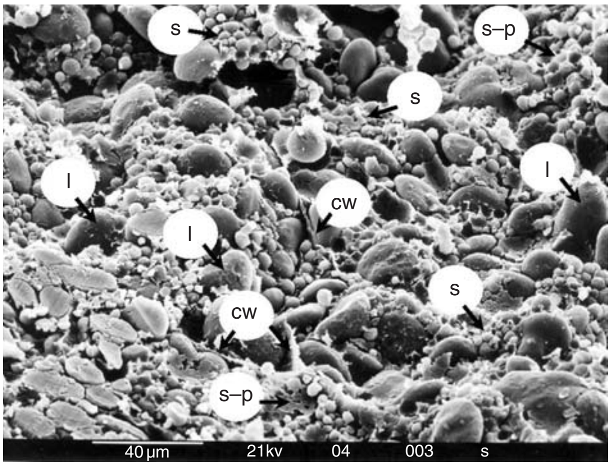

Figure 3 Starchy endosperm of wheat showing large and small starch granules and protein matrix. l – large starch granules; s – small starch granules; s–p – small starch granules and protein matrix; cw – endosperm cell wall.

malt is being used to convert cooked or gelatinized starch, the mashing temperature must be between 63°C and 65°C, temperatures at which malt starches (i.e., large starch granules) will gelatinize.

Malt contributes starch degrading enzymes such as α-amylase, limit dextrinase, and β-amylase during mashing. α-Amylase liquefies gelatinized starch molecules, β-amylase hydrolyzes these molecules to maltose – the main sugar of cereal-derived worts. Malt is an important source of amino nitrogen which yeast requires not only for growth but also for the production of flavor compounds. Shortage of amylolytic enzymes in the mash can be corrected by adding commercial amylolytic enzymes, if permitted. Malt contains vitamin B and phytic acid. The latter helps to cause an acidic pH during mashing which favors the activities of amylolytic and protolytic enzymes. Amino acids also add buffering capacity to the wort. Unmalted cereals also contribute amino acids and small assimilable peptides to the wort, albeit at significantly lower levels than malted barley.

Scotch whisky By law, only the enzymes of malted barley can be used to convert (hydrolyze) the starches of all malt mashes for malt whisky production and the enzymes of cooked maize or wheat used for grain whisky production. Whole grains of maize or wheat are cooked at ~140°C under pressure. Grits of maize or milled wheat are cooked at ~105°C under pressure. After these cereals are cooked and then cooled to ~63°C, a slurry of 9–10% milled green or dried malt is added to effect starch conversion into sugars.

The sugary wort required for Scotch malt whisky production is derived from a mash of 100% milled malt (e.g., 8–10 t). The malt is mashed in a water : malt ratio of ~4 : 1, at 63–64°C for at least 1 h. After the sugary wort is "run-off," the malt bed is washed, 2 or 3 times with hot water (80–100°C) to ensure that all the fermentable sugars are extracted.

Although some grain distilleries collect and ferment the sugary worts, others ferment the entire mash. To start the fermentation process, yeast is added to cooled worts (20°C) or to cooled unfiltered maize-malt or wheat-malt mashes (20°C). About 50% of the fermentable sugars of distillers' sugary worts are maltose. This sugar is mainly produced by β-amylase during mashing. However, α-amylase and limit dextrinase enzymes also assist in the hydrolysis of gelatinized (cooked/heated) starch – these enzymes facilitate the activity of the β-amylase enzyme. β-Amylase is more heat labile than α-amylase. β-D-glucans are present in the cell walls of the endosperm. Barley contains ~3.0% β-glucan. Malt should contain less than 0.4% β-glucan to ensure that during mashing, wort "run-off" rate and starch release are optimal. Cell wall β-D-glucans and pentosans can limit water removal from spent grains required for animal feed production. Appropriate treatment of spent grains with β-glucanase assists dewatering.

Irish whiskey In Ireland, a mash can contain only malt for malt whiskey production or the mash may have 60% of hammer-milled barley and 40% malt or it may comprise 90% hammer-milled maize and 10% malt. The 10% malt may be replaced by hydrolytic enzymes. Commercial enzymes can only be added to the production of grain whiskey. The different spirits produced are used to produce a wide range of distilled products such as malt whiskies or blends of malt and grain whiskies made in pot stills or continuous stills.

American whiskies Bourbon must be produced from a mash of not less than 51% corn but typically a bourbon mash contains ~70% corn, 15% rye, and 15% malted barley. A rye whiskey mash can contain 51% rye, 39% corn, and 10% malted barley. Tennessee whiskey can be made from a mash of 80% corn, 10% rye, and 10% malt. Different milling systems are used to mill the raw grain. The milled grains and malt or enzymes are heated and cooked and then cooled. An additional quantity of milled malt is mashed in at temperatures not exceeding 64°C. Highly enzymic malts are used. The quantities added are usually lower than those used in Scotch grain whisky production. During mashing, natural enzymes of the malt and commercial enzymes produce optimal conversion of starch to sugars. Conversion (mashing) time varies from 15 min to 60 min. The term, "sour mash," describes the acidic nature of the mash. Long mashing times can encourage the development of microbial infection. At the end of the mashing process, the mash bed (spent grains) is washed with hot water to optimize sugar release, as in other whisky-making processes.

Canadian whiskies For Canadian whiskey, maize grains are milled and cooked at 140°C. The mash is cooled to 100°C and amylase is then added. Malts containing amylases and commercial amyloglucosidase are added at 63–65°C to optimize fermentability. For Canadian rye whiskey, the mash contains milled rye alone or more commonly, rye and other cereals such as maize and/or wheat. Heat-stable amylase and β-glucanase enzymes are added as the mash is heated up to ~85°C where the grain meal is held for ~20 min. It is then cooled to 63–65°C and amylases and amyloglucosidases are added to give optimal release of sugars. Finally, the mash is cooled and yeast is added. Fermentation starts at 20–30°C. Yeast may have been subjected to lactic souring.

Gin and vodka The spirits used for the production of gin or vodka are usually neutral spirits. These are mainly highly distilled ethanol (minimum 96%) and are almost free of congeners. The main flavor product is ethanol. The lowest limit of ethanol for neutral spirit (96%) is usually higher than the 94% taken for the production of Scotch grain whisky. In this regard, Scotch grain whisky has more flavor congeners than the spirits used for gin and vodka production. Neutral spirits are produced from mashes of milled/cooked cereals, potatoes, molasses, fruits, or sugars. Mashes containing cereals and potatoes require the addition of malt enzymes or external enzymes to convert starches into sugars as described for whisky/whiskey production.

Cachaça For traditional Cachaça, e.g., "artesanal," no mashing process is necessary because the fermentation sugar, sucrose, is squeezed from washed, freshly harvested, stems as sugar cane juice. Many varieties of sugar canes are used; some reflect crosses of standard varieties such as *Saccharum officinarum* L. with other varieties. Sugar content of the juice is ~12–16%.

Rum The fermentation sugar, sucrose, is derived primarily from high or low sugar molasses. Sugar cane juice is also used. Molasses have a higher mineral and nitrogen content than sugar cane juice and impart a different flavor to the final product. Molasses of high sugar content (~22–24% sucrose), tend to produce a spirit of 10–12% ethanol, whereas sugar cane juice (12–16% sucrose) tends to produce a post-fermentation alcohol content of ~6–8% alcohol. Rum produced from sugar beet molasses gives a very different flavor from rum produced from sugar cane molasses. Tasting trials showed that the sugar cane product is generally preferred.

Tequila Tequila and mezcal (with or without the "worm" in the bottle) are both produced from the Agave plant. However, tequila is produced in Tequila and its vicinity from *Agave tequilana* Weber var. Azul, whereas mezcal is produced from *Agave patatorum*. Agave head is harvested and cut into pieces for cooking. During cooking, inulin polymer is hydrolyzed to produce fructose which is sweeter than sucrose – this process can take 2 days. Autoclave cooking will produce a sugar syrup of ~10%. The cooked agave is milled in small sugar cane mills and the milled product and sugary juices are collected.

For the production of 100% tequila, only agave sugar can be used. For other kinds of tequila, cane sugar, molasses, or corn syrups can be added to levels of 49%. The sugary worts used to produce 100% tequila have sugar concentrations that range from 4% to 10%. For other tequilas, sugar concentration can range from 8% to 16%.

Brandies:

1. Cognac derives its name from the town Cognac. The base wine for cognac production comes mainly from the St. Emillion grape although grapes from Folle Blanche and Columbard are authorized. The glucose sugar of the acidic wine is

fermented without the addition of yeast for 3–5 weeks. The acidic wine is then distilled in small pot stills.
2. Armagnac comes from the Armagnac region and there is written reference to this brandy in 1411, two centuries before cognac was produced. Grape sugar (glucose) is fermented to produce, like cognac, low-alcohol wines. These are then concentrated by distillation without prior removal of grape residues (lees).
3. Eau de vie – soft fruits are mashed (unheated or preheated) and their sugars are converted to alcohol during fermentation. Alcohol is concentrated in pot stills. Eau de vie is associated with the Alsace region. Calvados brandy, which is made from apple mashes, specifically comes from the provinces of Brittany, Normandy, and Maine.

Fermentation

Cereal (malt) worts can have the following composition of sugars and dextrins: fructose 1%; glucose 10%; sucrose 5%; maltose 50%; maltotriose 15%; maltotetrose 6%; and dextrins 13%. Excluding sucrose, these sugars are the products of amylolytic hydrolysis of gelatinized starch during mashing. In contrast, sucrose is the only major sugar of cane juice. In fruit mashes and juices, glucose and sucrose are the major sugars and in tequila mashes, fructose is the dominant sugar. Total sugar levels of distillers' wort range from 10% to 16%. Yeast requires a nitrogen source to effect expected growth from which ethanol and flavor compounds are produced (Figure 4). The raw materials used usually satisfy the nitrogen requirements of the fermenting yeast.

A malt whisky wort can contain $250\,\mathrm{mg\,l^{-1}}$ of α-amino nitrogen, whereas a grain whisky mash of 90% wheat can contain ~100–120 $\mathrm{mg\,l^{-1}}$. In malt whisky production, there is an exceptionally high level of amino acids which may contribute to the production of esters and other flavor compounds. The role of amino acids in the formation of flavor compounds is complex. However, optimal levels of these nitrogenous compounds will assist in optimal production of esters. Suboptimal levels of amino compounds may encourage the production of higher (fusel) alcohols. However, even at optimal levels of amino nitrogen compounds, different levels of esters can be produced suggesting that other factors influence ester production, such as yeast type, wort concentration, lipid content, and fermentation temperature. Special mention is made of esters because they are important flavor compounds that contribute different flavors to distilled spirits. In this regard, the total ester content does not convey the individual or the complementary contribution of different esters to overall flavor. Insufficient nitrogen nutrients can limit yeast growth, resulting in the production of unexpected or undesirable flavors.

One of the main distinctions in fermentation systems is fermenter size. Cachaça and brandies

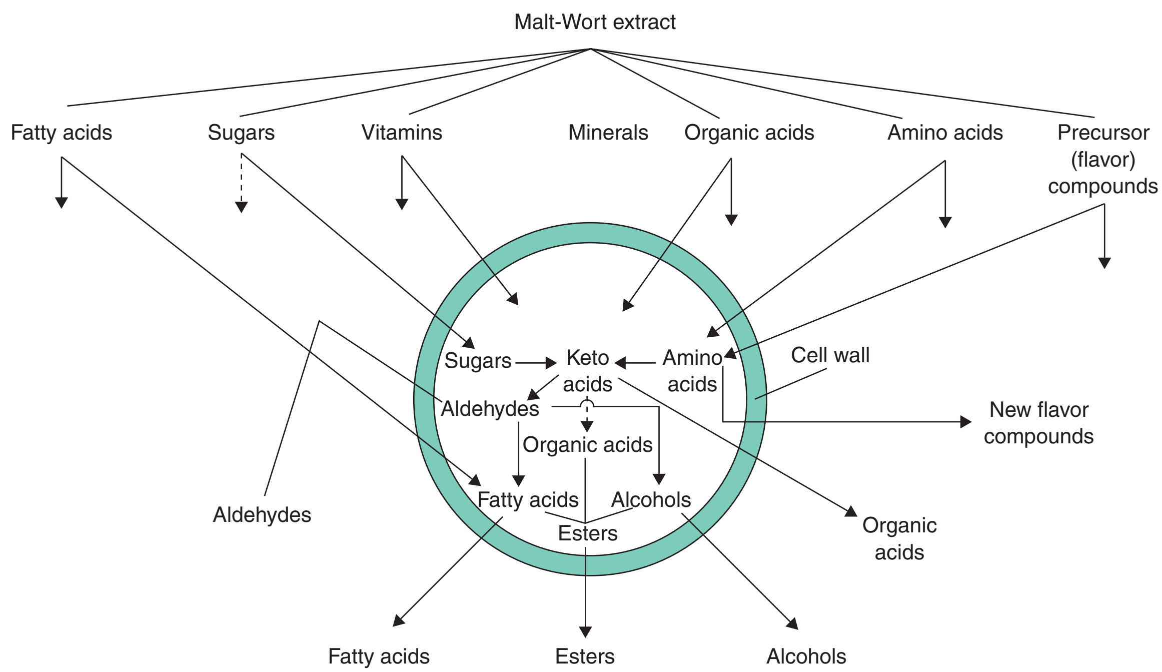

Figure 4 Fermentation: production of low percentage of spirit (6–8%) from plant sugars and nutrients prior to distillation.

such as cognac and armagnac are produced from small fermentation volumes (~1500–3000 l), whereas rum and tequila are derived from larger volumes in the order of 10 000–12 000 l. In malt distilleries, fermentation vessels can range in size from 4000 to 20 000 l. In grain distilleries, these vessels can be as large as 250 000 l. Yeast is usually added to initiate and advance fermentation in gin, vodka, rum, and whisky production. Residual postfermentation yeasts may be used to start new fermentations of spirits such as Cachaça, tequila, and some brandies. However, in cognac, wine is allowed to self-ferment for 3–5 weeks. For "artesanal" Cachaça, naturally trapped yeast is added initially to effect fermentation. In the production of heavy Jamaican rum, natural inoculation is encouraged but can be supplemented by yeast additions. In Scotch whisky production, fresh yeast is added to new fermentations.

Fermentation temperatures vary. Unlike beer fermentation, which usually takes place below 15°C, distillery fermentations range from 20°C to 40°C. Since there is no temperature control, whisky/whiskey fermentations can start at 20°C and rise to 30°C over a short 48 h period of fermentation. Most distillery fermentations are usually completed by 48 h, compared with beer fermentations which can extend to 5 days. However, in tequila and American whiskey production, slow fermentations may exceed 72 h. The high fermentation temperature and the high yeast-pitching rate are mainly responsible for the fast fermentation rates of most of these spirits. Pitching rates for yeast (*Saccharomyces cerevisiae*) vary and can range from ~10 to 20 million cells per ml. Distillers use either residual postfermentation yeast, company-cultured yeast, or purchased yeast to effect fermentation. Yeast under cold storage tends to be more viable that yeast stored at warm temperatures. Although, great efforts are made to control bacterial infection during fermentation, the by-products of the metabolism of lactic acid bacteria and *Clostridium saccharobutyricum* in heavy rum production, can be essential congeners of the expected flavor profile of fermented worts and mashes. In general, during fermentation, sugars such as sucrose, glucose, fructose, maltose, maltotriose, and maltotetrose are fermented to ethanol, and, nutrients (e.g., zinc and amino acids, vitamins, fatty acids), and some malt flavor compounds are used by the yeast to grow and form a wide range of flavor compounds characteristic of the spirit to be produced. These flavor compounds include simple alcohols and higher alcohols (fusel oils), esters, organic acids, aldehydes, ketones, sulfur compounds, and aromatic flavor compounds such as acetals which tend to develop in acid conditions and high ethanol medium.

At the end of the fermentation process, the chemical composition of mashes and worts could be similar. However, intraspirit and interspirit differences become distinct after the distillation process has isolated, separated, and combined the congeners that define particular spirit products. Fermented worts, derived from different raw materials, will produce different spirit products. However, within a product type, differences will be caused by differences in still sizes, shapes, and modes of operation. In this regard, distillation is as important as raw material in defining spirit type and spirit quality. Here, quality is defined as meeting the expectations of the customer.

Distillation

Distilling Using Copper Pot Stills

The fermented worts or mashes of many distilled spirits contain ~6–8% ethanol. The purpose of distillation is to vaporize the compounds present in worts and mashes and effect their separation and concentration. Still size can vary from 5000 to 25 000 l in capacity. Volatile compounds are derived from the contents of the still. New volatile compounds are also formed during distillation. If specific cyanide-containing precursors are present, unacceptable compounds such as ethyl carbamate are produced. Cereal spirits should have an upper limit of 150 $\mu g\,l^{-1}$ of ethyl carbomate; fruit spirits should have no more than 500 $\mu g\,l^{-1}$. Most stills are heated by heating coils. Cognac stills are fired directly. In the production of Scotch malt whisky, double distillation is involved but triple distillation occurs on a limited scale. The situation is similar for rums. For Irish whiskies, triple distillation is standard. Single distillation is also used to produce products such as Cachaça and armagnac. Double distillation usually takes place in wash and spirit stills. The distillate of the wash still (the low wine) is very high in congeners and ethanol is concentrated from 6–8% to ~23%. In the spirit still, the low wine is fractionated into "foreshots" (heads), "middle cut" (spirit), and "feints" (tails). Single distillation pot stills operate in a similar manner to spirit stills, separating the ferment into three factions. After maturation in wooden (e.g., oak) casks, the "middle cut" (spirits) will be transformed into the distilled product (Table 2). In the triple distillation system, as used for Irish whiskey, the late portion of the distillate of the wash still is removed and redistilled in a low-wine still. The early portion of the wash still distillate and the early portion of the low-wine still are added to the spirit still for fractionation in "heads," "middle cut," and "tails." As is the case for spirits such as Scotch whiskies and brandy, the congener levels of traditional Cachaça are higher than those of rum or bourbon. However, this may not be the case for all "industrial" Cachaça, produced in continuous stills.

The overlap of "foreshots" into the "middle cut" (i.e., the spirit) and the overlap of the "middle cut" into the "feints" can change the expected flavors of the spirit. High levels of "foreshot" compounds in the spirit can be detected by making a 50/50 mixture of spirit and water. If cloudiness develops, the "foreshot" content of the spirit is usually too high and adjustments to the "spirit cut" time should be made. "Foreshots" contain very volatile compounds which can confer "solvent-like" character to the spirit. In contrast, "feints" contain low volatile compounds that give the spirit a distinct stale, metallic odor.

During pot still distillation, ethanol concentration rises during "foreshot" collection but declines during the "middle cut" collection. Depending on still type, the total "middle cut" spirit fraction can contain 50–70% alcohol. Extended collection of the spirit fraction will lower its alcohol content and increase the possibility of having "feints" in the spirit. As regards the volatility of congeners: acetaldehyde, diacetyl, methanol, and some sulfur compounds are congeners of high volatility; esters of various kinds are congeners with medium volatility; fusel oils (i.e., higher alcohols) such as propanol, isobutanol, furfural, and isoamylalcohol have lower volatility than many esters but are usually more volatile than fatty acid congeners such as propionic, isobutyric, isovaleric, hexanoic, and octanoic acids. Despite differences in volatility, all these congeners can be found in the spirit, at levels that characterize the spirit type. The duration of collection of fractions containing these compounds is crucial as regards the distinctiveness and quality expectations of the spirit product.

Still size, shape, and distillation volume also affect the composition and levels of congeners present in the "middle cut" (i.e., spirit). The insertion of a water-cooled "purifier" between the neck of the still and the condenser also acts to reduce congener levels and lightens the spirit. The single distillation of Cachaça into "foreshots," "middle cut," and "feints" in small pot stills with cooling worms makes the middle cut spirit of Cachaça a distinctly different product from rum which is double distilled or triple distilled. Rums tend to have lower levels of flavor congeners. In general, in many spirits the fusel oils are in high concentration but do not dominate the overall aroma and taste because they are counter-balanced by esters and aldehydes.

Esters confer fruity and floral aromas to spirits and although esters are lost in the "foreshots," the levels retained in the "middle cut" (the spirit) are vitally important. In this regard, butanol, propanol, and aldehydes play important parts in giving distinctiveness to different spirits but when these congeners are balanced with esters and other flavor compounds, a more complex spirit is achieved. Phenol, cresol, and guaicaol compounds are derived from peated malts. These substances are distilled into the spirit and confer medicinal, smokey, and phenolic aromas and taste to Scotch malt whisky. The intensities of these compounds are balanced by congeners such as esters.

Methanol is regarded as an undesirable compound in spirits but is produced in high quantities in non-cereal mashes of plant tissue (e.g., potato, agave and fruits, Table 2). This highly volatile compound is dangerous to health and is absent from most distilled spirits but is present in "safe levels" in Eau de vie. It is a very volatile compound and should be removed in "foreshots" but fruit mashes contain high levels of pectin from which significant quantities of methanol are derived during mashing (extraction). Preheating of fruits to destroy the enzymes that release methanol or the fermentation of fruit juices instead of mashed fruits significantly reduces the levels of methanol produced.

Properties of copper in distilling The patina, which forms on the internal surface of pot stills, can function to reduce the levels of off-flavor sulfur compounds i.e., sulfides (e.g., dimethyl sulfide and mercaptans) from the spirit. Although copper can be detected in some spirits, the levels are within safe food levels.

Distillation Using Continuous Stills

Continuous stills are large vertical constructions. They contain internal sheets of copper which perform the same function as the copper in pot stills. In the Coffey stills there are two columns, the analyzer and rectifier. The 6–8% ethanol ferment or mash is heated as it passes down the rectifier. This heated mass then passes to the analyzer where steam is blown through it. Ethanol and flavor congeners are driven off. These pass back into the bottom of the rectifier and are collected at their designated heights from the lower plates to the higher plates of the rectifying column. For example, plates may ascend from 1 to 39: plate 7 is rich in isoamyl alcohol (fusel oils), plate 14 is rich in isobutyl alcohol, plate 23 is rich in n-propyl alcohol, plate 32 is rich in ethanol at ~94%. Ethanol concentration increases from plate 1 to plate 32. Volatiles such as methanol, sulfur compounds, and acetaldehyde are found in plates 35–39. An alternative type of continuous still is the column still. This comprises of a beer stripper where the 6–8% ethanol ferment is heated using stem, as in the analyzer. The vapors pass to the bottom of the concentrator which, like the rectifying column, fractionates the vaporized compounds at appropriate plates, for example: plate 5 (fusel oils, e.g., isoamylalcohol), plate 8 (propanol), plate 35 (ethanol, 95%), and the topmost plate 40 (methanol and volatile sulfur compounds). In all stills, condensers are connected to condense vapors that leave the still.

American whiskies are produced in continuous stills. They cannot be distilled above 80% ethanol and therefore contain more congeners than Scotch grain whisky at 94% ethanol and vodka and gin spirit at 96% ethanol. Canadian whiskies are produced from maize, rye, malted barley, and malted rye. Spirit fractions are collected between 65% and 95% ethanol and are used to produce different distilled products. Vodka and gin spirit (94% alcohol) may be passed through an extractive (water/steam) column still, which removes traces of volatiles such as methanol and diacetyl. The spirit is then concentrated in a rectifier where fusel oil is drawn off lower down the rectifier. The spirit is now at least 96% ethanol and is passed finally through a demethylizer to remove the last traces of methanol. In some plants, neutral spirit for vodka production is passed through charcoal to assist the purification process. During mashing, glycerol can be converted by lactic acid bacteria to acrolein which escapes during distillation causing an irritating pepper odor in the distillery.

Maturation

As indicated in Figure 5, distilled spirits are usually matured in wooden barrels for minimum periods of time. Some spirits are not matured such as vodka and gin, whereas, by law, Scotch whisky spirit and Irish and Canadian whiskey spirits are matured in oak casks for a minimum period of 3 years. American whiskies are matured for a minimum time of 2 years. The maturation periods for rums are variable – from, not at all (e.g., some light rums), to weeks or years, for heavy rums. Cachaça of the highest quality is matured in wooden barrels, especially oak and for at least 2 years. Brandies (e.g., cognac) are matured in oak barrels and, like Scotch whisky, can be matured for over 20 years. Maturation can take place in new, charred, wooden barrels (e.g., cognac or American bourbon whiskies) or in oak barrels previously used for sherry or bourbon. Port, madeira, and a variety of sherry barrels are now being used by some distillers to "finish" the maturation periods of their whiskies for wider brand appeal. Legally, tequila must be matured in oak casks for 2 months (rested tequila) or 1 year (aged tequila).

Different oak species are used for barrel construction, e.g., *Quercus ruber* (English), *Quercus petraea* (Spanish or French), or *Quercus alba* (USA). Barrel staves are sawn so that the normal tangential loss of water from the tree stem is avoided. Different spirits are filled into barrels at different strengths of ethanol. Spirit strengths of ~63.5% ethanol are most

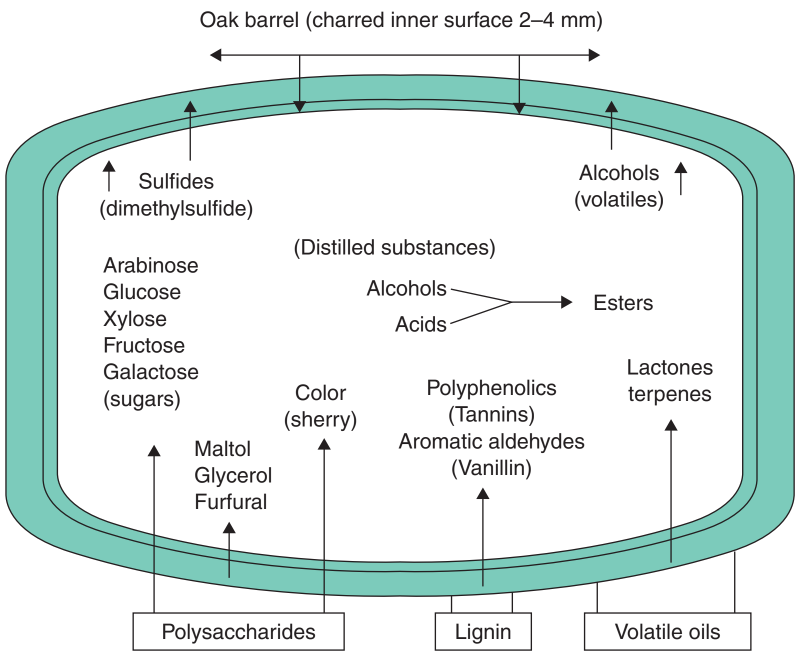

Figure 5 Maturation of distilled spirit ("middle cut") in oak barrels.

extractive. Temperature conditions influence maturation rate and maturation results. High temperature accelerates ethanol loss from barrels. For Scotch whisky, which can only be matured in oak casks, a loss of ~2% ("the angels' share") of the contents of the barrel occurs each year. In such maturation conditions, from an initial fill of 63.5% ethanol, ~58% ethanol will remain after a maturation period of 12 years. During maturation, unpleasant compounds are extracted by the barrel; pleasant compounds are released into the spirit and various important flavor compounds such as esters are formed in the spirit (Figure 5). The active charred inner surface of the barrel contains carbon which absorbs the unpleasant flavors of dimethylsulfide, dimethyldisulfide, methional, and methional acetate from the whisky, but not dimethyltrisulfide which, even at low concentrations of 4 ppb can be detected organoleptically (i.e., by taste or smell). From the scorched subsurface, important wood complexes are released into the spirit, adjusting its flavor, aroma, and increasing its color. Hydrolyzable tannins released into the spirit promote oxidative reactions such as ester formation between alcohols and acids.

Lignin is the strengthening material of wood and is a complex polymer which, when scorched by charring, releases aromatic aldehydes into the spirits such as vanillin and coniferaldehyde. Vanillins confer vanilla-like aromas to the spirit. Vanillin levels are very high in new barrels after charring and are characteristic flavors of bourbons and cognac. Other spirits that are matured in ex-bourbon casks also have detectable levels of vanilla-like aroma and taste. Low-level sweetness is conferred by the release of simple compounds such as glycerol and monosaccharide sugars such as xylose, arabinose, and glucose. Dry toasted malting flavors come from the release of furfural and maltol. American oak barrels release more lactones into the spirit than Spanish oak barrels. *Cis*-lactones confer desirable woody aromas and sweet, smooth, coconut flavors. Components of tannins such as gallic acid and ellagic acid can contribute astringency and can be oxidized to give color and fragrant compounds. The solid matter content of whisky increases by $\sim 2.5\,\mathrm{g\,l^{-1}}$ over a period of 12 years. Some of this material is lipid material (fatty acid esters) that will form hazes when water is added to matured spirit products, if such products are not cold filtered. Cask strength Scotch whiskies which are not filtered tend to form hazes when water is added. Metal ions can also form flocs, which are removed by filtration of the product. Pieces of charcoal that are dislodged from the charred surface of the barrel are also removed during filtration. The sherry flavors and vanilla flavors of distilled products are derived from the barrels in which they are matured. Sherry barrels also contribute color to maturing spirits.

Repeated use of a barrel will deplete its reservoir of color-producing materials and flavor compounds, and its ability to remove undesirable compounds such as sulfides. Such barrels are rejuvinated by scraping away the inner carbon surface and recharring the newly exposed wood. A barrel may last as long as forty years. However, its effectiveness declines over these years. Maturation moderates the volatility and increases the smoothness of the spirit. This is particularly important in high congener spirits.

Blending and Bottling

Before blending or vatting, the spirit is checked before the casks are emptied and collected in tanks. In general, whiskies, Cachaça, rums, brandies, or tequila are vatted and left to "marry" before being reduced with water of low mineral content to bottling strength. The ethanol levels of vodka and gin are also reduced using low mineral water. Judicious vatting (mixing) of cognac of different ethanol concentrations is effected to arrive at the bottling strength required. The mixing of generic spirits can be referred to as vatting. However, blending is used to describe the mixing of different kinds of spirits (e.g., malt and grain whiskies). In this regard, malt whiskies can be described as "pure" single malts (malt whisky from one distillery), "pure" malts (mixture (vatting) of different malt whiskies), or "blends" of malt and grain whiskies. Here, pure is taken to mean of one kind. The mixing of Cachaça products from different production operations is equivalent to the vatting of single malts because the Cachaça products used are different in character but are produced traditionally and are therefore of one kind. In contrast, in America, blended whiskies will contain grain whiskey, neutral spirit or light whiskey and a complement of heavy whiskey or whiskies such as bourbon or maize whiskey. These heavy whiskies are called "straights" if matured for more than 2 years. As in Ireland, the mash bill and still type determine the types of whiskies that are blended: such as products of high congener levels (malt or high malt whiskies) and products of low congener (high grain whiskies) levels. In Canada, light whiskies, made from rye and malted barley and malted rye, in continuous stills are blended with high flavor corn whiskies (65–80% ethanol), made from ~60% corn (maize), rye, and malted barley in either pot stills or continuous stills. Some Canadian whiskies are blended with wines, sherries, brandies, rums, bourbons, and malt whiskies to create different flavors and aromas. Lighter whiskies may be used in larger quantities than heavier spirits; they may not only add lightness but also add flavor notes of freshness, which are crucial to the "drinkability" of blended whiskies.

Since blended whiskies, e.g., Scotch blends, can contain as many as 30–40 malt whiskies and ~6–8 grain whiskies, the overall complexity is greater than any comparable single malt. Blending extends product range and provides the possibility of arriving at new products which the public may prefer. This can take a long time; but the opportunity of developing new products should not be ignored. The levels of important congener compounds (e.g., esters) may not be reduced by blending because very highly flavored whiskies in the blend can compensate for reduction of esters by dilution with grain whiskies which have low congener levels. In this regard, some blended Scotch whiskies can have similar ester contents to malt whiskies, even though a malt whisky may have 4–5 times as many esters as a grain whisky. Blending is the high art of distilled beverage production, providing the customer with consistency and complexity without losing the high traditional qualities of a wide range of individual products which are blended together to extend drinkability.

Conclusion

Reference has not been made to the by-products of the distillation process. In some plants (e.g., Scotch grain whisky) carbon dioxide is collected and sold, spent grains from the mashing process and spent materials from the distillation process (stillage) are dried and sold as animal feed. Wastewater (backset) is kept hot (e.g., 65–95°C) and reused as part of the mashing-in liquor or part of the cooking liquor. This liquor contains lactic acid. It is acidic, nutritious, and is a contributing factor to the term "sour mash" in American whiskey production. In addition, fusel oils are collected during the production of grain whisky and sold to the perfume industry. Waste sugar cane skins and fiber (bagasse) are used as fuel. These practices show that the distilling process is "environment friendly" because most of the products of the process are recovered and sold. Copper in the stillage can be problematic in animal feed but this is primarily a problem for single gut animals. The use of caramel of the highest quality is permitted in the industry to adjust the color of spirit products to expected levels. In most cases, very small levels are used compared with the very high levels used in, for example, chocolates, cola, and gravy mixes. In general, distilled beverages are ethanol-based products which are made with sound science and high art and, from the levels of their sales worldwide, are not only pleasant to drink, they also play an important part in defining the culture from which they originate. Those who produce them are proud of their distinctiveness and quality. An example of such pride can be found in Robert Burns' poem, "John Barleycorn," which accurately describes the production of Scotch whisky and glorifies its virtues – virtues Burns described collectively as a "cup of kindness" in the universal New Year's song, "Auld Lang Syne." He believed passionately that whisky and "freedom" went together. Maybe the same beliefs could be extended to other spirit beverages that reflect historical custom and practice (culture).

In order to protect standards of production and cultural heritage, the essential features of production of distilled spirit beverages should be enshrined in the law, as is the case for many of the distilled beverages described in Tables 1 and 2. In this regard, original place of production, raw material used, production process employed and overall aroma and taste should be taken into consideration. The spirit industry has always encouraged moderate drinking because it is fully aware that excessive alcohol consumption can cause health and social problems. The value of moderate consumption of alcohol, as regards improved cardiovascular function, is still being researched but the results so far are encouraging. Although, the production of distilled spirit beverages sustains many jobs and creates high tax returns to various governments, their contribution to the culture of celebration is probably their most important merit in society.

See also: **Beverages**: Asian Alcoholic Beverages. **Fermentation**: Foods and Nonalcoholic Beverages.

Further Reading

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Relevant Websites

No specific websites are listed. Most companies producing distilled beverages include some technical information on their product. In particular, interesting images of production processes can often be found.

BREADS

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Introduction

Bread, in one form or another, has served as mankind's Staff of Life for centuries. Its ability to provide sustenance to the human body is remarkable, as evidenced by analysis of its dietary components. While many people around the globe think of bread as simply a staple of the daily diet, it is much more than that to many others. To the wheat breeders, farmers, millers, and bakers of the world, bread is a means of providing for themselves and their families, a product to be proud of, and practically a way of life.

As would be expected of a product that has been in existence for so long, bread has evolved over the years such that it means different things to different people. Indeed, the geographical and cultural differences in the product known as "bread" are quite broad, as evidenced by the tremendous array of bread varieties available today in just the North American market. Pan breads, hearth breads, buns and rolls, and flat breads are increasingly available around the world, even if they are not indigenous to the consumer's homeland. Simply put, the differences between breads are largely a function of the ingredients used, and the manner in which these ingredients are processed into the final product.

Ingredients

Various ingredients are used in bread formulas to manipulate the characteristics of the finished product. As man has learned over time, only two ingredients are absolutely necessary to make a palatable loaf of bread, those being wheat flour and water. As time went by and man learned more about his surroundings, he discovered that salt and yeast added flavor and lightness to his bread. Today, additional ingredients are used in bread to meet the demands of the modern-day consumer, namely, better keeping qualities, better flavor, softer (or firmer) texture, and other physical and sensory improvements. As mentioned previously, geographical and cultural differences exist between breads, meaning that ingredients that are commonly used in North American, British, and Australian pan breads may not be used in German rye bread, French baguettes, or Arabic bread, for example. See **Table 1** for common ingredients and their functionality.

Equipment

As detailed in **Bakeries**, the modern commercial bakery houses many pieces of specialized equipment. The goal of using modern automated equipment is to carry out the basic steps of the dough production process in bulk quantities, and to do it profitably. Equipment design, construction, and usage is truly global, with bakers all over the world buying and using equipment made in foreign countries. See **Table 2** for an overview on equipment used for modern bread production.

Dough-Making Processes

Whether bread is made by hand or by machine, certain steps of the bread-making process are the same. Bread owes its uniqueness not only to the ingredients and equipment used in its manufacture, but also to the different processes by which dough is made. Most of these processes are of geographical or cultural origin, and are still practiced in the areas of their founding today. However, with globalization of trade and world travel, consumers now demand products that were not familiar to them in the past. It is not difficult to find authentic French bread in America, flour tortillas in Australia, or pita bread in Hong Kong. However, achieving the unique characteristics of different breads often requires that a specific dough-making process be used.