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CHEMICAL PROCESS INDUSTRIES

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liquid layers, represented in Fig. 31.3 by points *M* and *N*. The ratio of the top layer *N* to the bottom layer *M* is equal to *MF/FN*, or 84:16. The compositions involved are shown on Fig. 31.4, which also illustrates how this process functions. These same principles of distillation in multicomponent systems, involving constant boiling mixtures, are used for dehydrating other organic liquids, such as propyl alcohol, and for removing the water formed in sulfonations (benzene-sulfonic acid) and esterifications (ethyl acetate).[1] The fundamentals of distillation are here presented because of the extensive data on alcohol that are available.

BEERS, WINES, AND LIQUORS

The making of fermented beverages was discovered by primitive man, and has been practiced as an art for thousands of years. Within the past century and a half this has evolved into a highly developed science. As Muspratt writes, "There is no department of the arts and manufactures where chemistry has exerted a more decided influence than in brewing." But E. A. Siebel adds to this, "A modern brewer has to be an engineer, a chemist, and a bacteriologist." In common with other food industries, the factors of taste, odor, and, almost, of individual preference exist, to force the manufacturer to exert the greatest skill and experience in producing palatable beverages of great variety. In the last analysis, the criterion of quality, with all the refinements of modern science, still lies in the human sensory organs of taste, smell, and sight.

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USES AND ECONOMICS As Table 31.3 indicates, many millions of barrels of alcoholic beverages are manufactured in the United States each year.

RAW MATERIALS Grains and fruits supplying carbohydrates are the basic raw materials. The variety of grains and fruits employed is wide, changing from country to country or from beverage to beverage. Russia ferments potatoes and by distillation obtains vodka; similar treatment of the sap of the maguey in Mexico yields pulque; but the world's chief raw materials for fermentations are the cereals, corn, barley, and rice, together with the grape.

MAKING OF BEER[2] Beer and allied products are beverages of low alcoholic content (2 to 7%) made by brewing various cereals with hops, usually added to impart a more or less bitter taste and to control the fermentation that follows. The cereals employed are barley, malted to develop the necessary enzymes and the desired flavor, as well as malt adjuncts: flaked rice, oats, and corn, with wheat used in Germany and rice and millet in

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[1] See Perry, sec. 13, on distillation, for a rigorous and fundamental treatment of this important unit operation.

[2] [illegible] and Weissler, Brewing, *I&EC*, 43, 1262 (1951) (many excellent pictures, tables, and diagrams); ECT, 2d ed., vol. 3, p. 297, 1964.

TABLE 31.3 *U.S. Production of Alcoholic Beverages, Fiscal Years 1939, 1950, 1963–1965 (In thousands)*

Beverage	*1965*	*1964*	*1963*	*1950*	*1939*
Still, wine gal	197,257	200,572	191,220	297,857	231,986
Sparkling, wine gal	6,358	5,305	4,485	21,225	6,634
Distilled, proof gal	92,923	88,033	87,617	107,951	43,401
Fermented, bbl	108,015	103,018	97,961	98,807	53,571
Cereal, bbl	73	57	35	45	63

Source: U.S. Treasury, Internal Revenue. *Note:* bbl contains 31 gal.

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China. Brewing sugars and sirups (corn sugar, or glucose) and yeast complete the raw materials. For beer the most important cereal is barley, which is converted into malt by partial germination.[1]

The barley is steeped in cold water and spread out on floors or in special compartments and regularly turned over for from 5 to 8 days, the layers being gradually thinned as the germination proceeds. At the proper time, when the enzymes are formed, the growth is arrested by heat. During the growth, oxygen is absorbed, carbon dioxide given off, and the enzyme *diastase* formed. This latter is the biological catalyst that changes the dissolved starch into the disaccharide maltose which, after transformation into the monosaccharide glucose by the *maltase* enzyme, is directly fermentable by yeast.

The flowchart for beer in Fig. 31.5 may be divided into three groups of procedures: (1) brewing of the mash through to the cooled hopped wort, (2) fermentation, and (3) storage, finishing, and packaging for market. *Mashing* is the extraction of the valuable constituents of malt, malt adjuncts, and sugars by macerating the ground materials with 7.5 to 9 bbl of water per 1,000 lb of materials listed in Fig. 31.5 and water-treated to prevent too high pH, which would tend to make a dark beer. In the pressure cooker the insoluble starch is converted into liquefied starch, and the soluble malt starch into dextrin and malt sugars. The resulting boiling cooker mash, mixed with the rest of the malt in the mash tun, raising the temperature to 168 F, is used to prepare the brewers' *wort*.[2]

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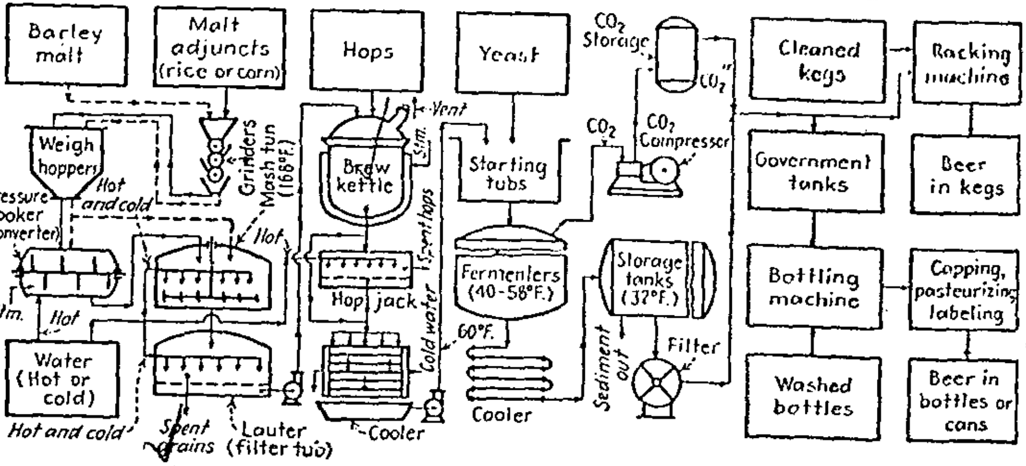
[1] Brewing of Lager Beer, *Chem. & Met. Eng.*, 49 (7), 112 (1942) (pictured flowchart); cf. ECT, 2d ed., vol. 2, pp. 384–413; Staff Industry Report, Beer, *I&EC*, 43, 1264 (1951); Chopey, What's Doing in Beer Brewing?, *CE*, 69 (13), 94 (1962) (process flowchart with pictures); continuous-flow beer making is now practiced (1964) by Carling in Fort Worth, Tex.; Continuous Beermaking, *CE*, 72 (1), 18 (1965).

[2] The wort is the liquid resulting from the mashing process, i.e., the extracting and solubilizing of the malt and malt adjuncts. Wort composition varies from 17 to 24% solids by weight for the first wort to approximately 1% solids for the last wort removed by the sparge water.



Brewer's malt	35-38 lb.
Malt adjuncts	12-14 lb.
Hops	½-1¼ lb.
Yeast	¾-1 lb.

Brewery labor	$0.50-$1.50	Per U.S. barrel (31 gal.) of beer
Power and steam	0.50-0.70	
Bottling costs (labor labels, alkali, etc.)	1.50-2.50	

Fig. 31.5 Flowchart for manufacture of beer.

This is carried out in the mash tun. After all the required ingredients have been dissolved from the brewing materials, the entire mash is run from the mash tun to filter presses or the lauter or straining tub, where the wort is separated from the insoluble spent grains through a slotted false bottom and run into the copper wort cooker. For complete recovery of all substances in solution, a spray of decarbonated water at 165 F is rained through the grains. This is called *sparging*.

The wort is cooked for approximately 3 hr, during two of which it is in contact with hops. The purpose of boiling is to concentrate the wort to the desired strength, to sterilize it (15 min) and destroy all the enzymes, to coagulate certain proteins by heat (180 F), to modify the malty smell of the wort, and to extract the hop resins' tannin and aroma from the hops, which are added during the cooking process. At the end of the 3 hr the spent hops are separated from the boiling wort very quickly through a false bottom in the hop jack or strainer underneath the copper cooker. Since the spent hops retain 3 bbl of wort per 100 lb of hops, they should also be sparged. The wort is then ready to be cooled.

The cooling step is not only to reduce the temperature, but also to allow the wort to absorb enough air to facilitate the start of the fermentation. In addition, the protein and hop resins are precipitated. The hot wort may be first cooled to about 150 to 160 F in a large shallow cooler, where certain of the resins precipitate. The wort is then run over the horizontal, brine-cooled copper tubes of the open Baudelot cooler or through a shell and tube heat exchanger,[1] where aeration also takes place. Slight concentration, due to evaporation, occurs. This operation is performed under controlled conditions to prevent contamination by *wild* yeasts. Frequently, sterilized air is used.

The cooled wort is mixed with selected yeasts in the line leading to the starting tubs, between $\frac{3}{4}$ and 1 lb of yeast being used per barrel of beer. The initial *fermentation* temperature is 40 to 43 F, but as the fermentation proceeds, the temperature rises to 58 F. This is easily explained by the fact that the conversion of the sugar to CO_2 and ethyl alcohol by the enzymes of the yeast generates 280 Btu/lb of maltose converted. The temperature is partly controlled by attemperators inserted in the fermentors. The mixture is skimmed to remove the foreign substances that the evolved carbon dioxide brings to the top. Thus it is quite evident that a steady evolution of gas is necessary to cleanse the beer properly. The CO_2 evolved is collected by using closed fermentors and stored under 250 lb pressure for subsequent use in carbonating beer.

The yeast gradually settles to the bottom of the tub, so that at the end of 7 to 10 days the fermented beer is ready to be vatted. The liquid is very opalescent in appearance, under a cover of foam. As the beer leaves the fermenting cellar, it contains in suspension hop resins, insoluble nitrogenous substances, and a fair amount of yeast. The beer is cooled to 32 F, and stored in the cellar for 3 to 6 weeks at this temperature. During this period, clarification, separation, and precipitation of hard resins and improvement in palatability (mellowing) occur. At the end of the period the beer is carbonated[2] and pumped through a pulp filter with or without such non-taste-imparting filter aids as asbestos fiber. In the United States, public demand favors a brilliant beverage. As a result, the beer is sometimes refiltered through cotton pulp, keeping carbon dioxide on the entire system. About 97 bbl of beer is produced per 100 bbl of wort in the starting tubs. After bottling, the beer is pasteurized at 140 F.

[1] Cf. Quepy, *op. cit.*

[2] The carbon dioxide should be kept free from air, which would interfere with the stability and quality of the beer. The gas is pumped in close to 32 F and amounts to between 0.36 and 0.45% of the weight of the beer.

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AP-42 Section 9.12.1
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31 FERMENTATION INDUSTRIES

ployment of microorganisms to convert one substance into another is a science that assiduously studying and is energetically applying. Although the fermentation of alcohol was known to primitive man, and although the making of various bever- of fruits and grains has been well established for centuries, it is only during the generation that the wider application of this procedure has been recognized. Now directing the life processes of yeasts, bacteria, and molds to the production of chemi- Alcohol can be viewed as having been produced in this way from the earliest times, making of acetone and butanol, of acetic acid, lactic acid, citric acid, and the antibiotics are recent technical accomplishments.

foundation of the scientific understanding of fermentation, indeed of the action microorganisms, and hence of their economic control, rests firmly upon the genius Louis Pasteur.[1] He showed that fermentation is directly caused by the life of minute organisms. By understanding how these microorganisms function and recognition that varieties of yeasts, for instance, act differently and that environ- fundamentally affects even a given strain, one can control these processes of fermen- an exact scientific manner.

fungi are a branch of the nongreen plants and include bacteria, yeasts, and These feed upon organic materials. It is this feeding that interests the manufac- if he supplies to certain yeasts, bacteria, or molds the necessary fundamental food, together with the other needed nutrients, these microvegetative organisms only grow and multiply but will change the food into other chemical substances. Yeasts and bacteria are unicellular and of very small dimensions. The yeasts are oval and perhaps 0.004 to 0.010 mm in diameter. The bacteria are smaller, than 0.007 mm in the longer dimension, and more diverse in shape. Many the bacilli, are rod-shaped. The yeasts multiply by budding, and the bacteria by sion. The molds are multicellular filaments and increase by vegetative growth of nt. Sporulation provides for the next cycle, as it does also with many bacteria. tative reproduction cycle of these bacteria and of the yeasts is short—measured Because of this, they multiply exceedingly fast.

microorganisms have been brought into useful service to man. One of the developments since the 1920s has been the extension to the making of chemicals, alcohol, of the life processes of these minute vegetative organisms. Table 31.1 these performances, which, in larger industrial scale, embrace the manufac- enzymes, acetone, butanol, acetic acid, lactic acid, and citric acid. This importance of fermentation in foods and feeds. Several of the older labora- tories, such as the making of citric and gluconic acids, have been developed to al stage. One of the outstanding developments of World War II was the making which stimulated further important discoveries in the field of antibiotics.

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[1] Boruff and Van Lanen, Fermentation, *I&EC*, 43, 574 (1951); ECT, vol. 6, pp. 317–375, pp. 332–336 for industrial applications (62 refs.) 1951; *ibid.*, vol. 8, pp. 871–880, CW Report, *CW*, June 16, 1962, pp. 97–112; Koshland, Correlation of Structure and Action, *Science*, 142, 1533 (1963).

Many fermentation processes are frequently in direct competition with strictly chemical syntheses. Alcohol from fermentation and from ethylene compete. Acetone, butanol, and acetic acid by fermentation have largely been superseded by their synthetic counterparts. However, the antibiotics have paced a recent fermentation revival, and with the exception of one, chloramphenicol, all the major antibiotics are obtained exclusively from fermentation processes. Dextran[1] is another fermentation product which, because of its possible use as a plasma volume expander, has gained prominence. The microbiological production of vitamins has also become economically important. In Chap. 40 antibiotics, hormones, and vitamins are presented, together with several flowcharts. See Fig. 40.6 for penicillin, erythromycin, and streptomycin.

Actually, fermentation under controlled conditions involves *chemical conversion.*[2]

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[1] Bixler *et al.*, Dextran, *I&EC*, 45, 692 (1953).

[2] Wallen, Stodola, and Jackson, Type Reactions in Fermentation Chemistry, Dept. of Agriculture, Agricultural Research, 1959 (hundreds of reactions under 14 types); Gaden, Fermentation, *CE*, 164, April, 1956.

TABLE 31.1 ***Survey of Important Fermentations***

Food and feed	*Industrial, pharmaceutical*	*Laboratory*
Bread (Y)	Alcohol (Y)	Succinic acid (M, Y, and B)
Cheese (M or B)	Yeast (Y)	Fumaric acid (M)
Vinegar (B and Y)	Carbon dioxide (Y)	
Sauerkraut (B)	Lactic acid (B)	Butyric acid (B)
Koji (M and Y)	Gallic acid (M)	Propionic acid (B)
Tea (B)	Glycerol (Y)	Malic acid (M and Y)
Coffee (M)	Acetic acid (B)	Fuel gas, H_2 (B)
Cocoa (B and Y)	Acetone-butyl alcohol (B)	
Pickles (B and Y)	Citric acid (M)	Acetic acid from cellulose
	Tartaric acid (Y)	
Olives (B)	Gluconic acid (M)	
Yeast (Y)		Proteins from petroleum
Tobacco	Sulfuric acid from sulfur (B)	
Glutamic acid (Chap. 27):		
Beer (Y)	Precipitation iron (B)	
Wine (Y)	Nitrogen fixation (B)	
Whisky (Y)	Fusel oil (Y)	
Vitamins	2,3-Butanediol (B)	Various antibiotics (Chap. 40)
Vitamin A(B)	Itaconic acid (M)	
Riboflavin (B and Y)	2-Ketogluconic acid (B)	
Vitamin B_{12} (B and M)	5-Ketogluconic acid (B)	
Ergosterol (Y and M)	Penicillin (M)	
Vitamin B_2 (Y)	Streptomycin (M)	
Antibiotics (Chap. 40)	Chloramphenicol (M)	
Penicillin (M)	Aureomycin (B)	
Aureomycin (M)	Terramycin (B)	
Terramycin (M)	Bacitracin (B)	
Bacitracin (B)	Neomycin (M)	
Hormones	Dextran (B)	
Enzymes	Lysine (B)	
Invertase	Dihydroxy-acetone (B)	
Zymase		
Amylase		
Diastase		
Maltase		

Y stands for yeast; B, for bacteria; M, for molds.

Some of the more important processes are *oxidation*, e.g., alcohol to acetic acid, sucrose to citric acid, and dextrose to gluconic acid; *reduction*, e.g., aldehydes to alcohols, as acetaldehyde to ethyl alcohol and sulfur to hydrogen sulfide; *hydrolysis*, e.g., starch to glucose or sucrose to glucose and fructose and on to alcohol; and *esterification*, e.g., hexose phosphate from hexose and phosphoric acid. Actually, certain chemical conversions can be carried on more efficiently by fermentation than by chemical synthesis.

Many of the chemical reactions caused by microorganisms are very complex, however, and cannot easily be classified; so the concept of fermentation itself as a chemical conversion has been developed. According to Silcox and Lee,[1] the five basic prerequisites of a good fermentation process are

1. A microorganism that forms a desired end product. This organism must be readily propagated and be capable of maintaining biological uniformity, thereby giving predictable yields.
2. Economic raw materials for the substrate, e.g., starch or one of several sugars.
3. Acceptable yields.
4. Rapid fermentation.
5. A product that is readily recovered and purified.

According to Lee, certain factors should be stressed in relation to the fermentation chemical-conversion or unit-process concept, such as microorganism, equipment, and the fermentation itself. Certain critical factors of the fermentation are the pH, temperature, aeration-agitation, pure-culture fermentation, and uniformity of yields.[2] The microorganisms should be those which flourish under comparatively simple and workable modifications of environmental conditions. See also the symposium on engineering advances in fermentation practice.[3]

In understanding, and hence in correctly handling microorganisms, a sharp differentiation should be made, usually, between the initial growth of a selected strain of these organisms to a sufficient quantity and the subsequent processes whereby, either through their continued *living* or as a result of *enzymes* previously secreted, the desired chemical is manufactured. To get a maximum chemical yield, it is frequently advisable to suppress additional increase in quantity of the microorganism. Highly specialized microbiologists working in well-equipped laboratories are engaged in selecting and growing the particular strain of the organism that experiment has shown to produce the chemical wanted, with the *greatest yields* and the *least by-product* and at the *lowest cost*.

No longer will just any yeast do to make industrial alcohol or a fermented beverage; not only are wild yeasts excluded, but a special strain must be used.

The yeasts, bacteria, and molds employed require specific environments and foods to ensure their activities. The concentration of the sugar or other food affects the product. The temperature most favorable varies (5 to 40 C). The pH also has great influence. Indeed, the bacteriologist has developed some acid-loving yeasts, so that the *wild yeasts*,

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[1] Fermentation, *I&EC*, **40**, 1602 (1948); Lee *et al.*, *I&EC*, **41**, 1868 (1949); **42**, 1672 (1950); **43**, 1948 (1951); **44**, 1996 (1952). The fermentation section of these annual unit process *reviews* should be especially consulted, the 1962 one being Humphrey *et al.*, Fermentation Process Technology, *I&EC*, Annual Review Supplement, pp. 66–76; cf. ECT.

[2] Humphrey *et al.*, Fermentation, *I&EC Unit Processes Review*, *I&EC*, **53**, 934 (1961) (excellent), and Annual Review Supplement, *ibid.*, 1962, p. 66; Phillips *et al.*, Oxygen Transfer in Fermentations, *I&EC*, **53**, 749–754 (1961); Deindoerfer and Humphrey, Mass Transfer from Individual Gas Bubbles, *I&EC*, **53**, 1755–1759 (1961).

[3] Eight articles, in *I&EC*, **52** (1), 59–66 (1960), and in Applied Microbiology, vol. 3, Academic, 1960.

not liking this condition, do not flourish. Some microorganisms require air (aerobic), and others go through their life processes without air (anaerobic). Certain anaerobes will neither grow nor function in the presence of air. In directing these minute vegetative organisms, conditions can be controlled to encourage the *multiplication* of the organism first, and then its *functioning*, either directly or through the *enzymes* secreted. How important this is can be seen from the knowledge that to grow 1 g of yeast (dry basis) requires 1.5 to 2.0 g of monosaccharide per day, and 6 g to maintain the yeast. By virtue of this growth, organic catalysts, or *enzymes*, are frequently formed that *directly cause the desired chemical change*. During the growth period, in addition to the primary, or energy food, such as monosaccharides for yeast, various *nutrients* are needed, such as small amounts of phosphates and nitrogenous compounds, as well as the favorable pH and temperature. Finally, certain substances will poison these useful little vegetables and their enzymes. Even the alcohol formed by the yeasts will eventually reach a concentration (varying with the yeast from about 2 to 15%) that will suppress the activity of the organism and of the enzymes. We are, furthermore, recognizing the importance of the life processes of the microorganisms in making vitamins, some of which are being recovered and sold in a concentrated form. "As with all life, the activities of microorganisms can be reduced to a consideration of enzymes acting on a substrate."[1]

INDUSTRIAL ALCOHOL

Industrial alcohol was an outgrowth of alcoholic beverages, but now it has become important by virtue of its economically useful properties as a solvent and for synthesis of other chemicals. Alcohol is sold as tax-paid[2] alcohol or, much more widely, as nontaxed denatured alcohol. There are two classes of the latter: completely denatured and specially denatured alcohol. The *completely denatured* formulas comprise admixtures of substances which are difficult to separate from the alcohol and which smell and taste bad, all this being designed to render the alcohol nonpotable. Such completely denatured alcohol is sold widely without bond. The public uses it as an antifreeze, and the factories find it an essential raw material. A typical completely denatured alcohol formula follows:

Formula No. 18. To every 100 gal of ethyl alcohol of not less than 160 proof add:

0.125 gal of Pyronate or a compound similar thereto.

0.50 gal of acetaldol (β-hydroxy-butyraldehyde), 2.50 gal of methyl isobutylketone, and 1.00 gal of kerosine.

The Federal government has recognized the needs of industry for alcohol in such form that it can enter into specialized manufacturing processes where the denaturants used in the completely denatured alcohols would interfere. So, since 1906, when the first U.S. denatured-alcohol law was passed, many formulas, of *specially denatured* alcohol, have been approved by the Federal

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[1] McGraw Hill Encyclopedia, vol. 7, p. 84, 1966.

[2] The Federal tax is $10.50 per proof gallon, and hence $19.95 on a gallon of 190-proof alcohol. To this the state may add its own tax, which in 1962 averaged $1.87 per proof, or tax, gallon. The total sum collected by the Federal Alcohol Tax Unit was $772,637,940 during the fiscal year 1965, largely from beverages. A *proof gallon* (tax gallon) signifies a gallon containing 50% alcohol by volume; 100 volumes of 100-proof alcohol contain 50 volumes of absolute alcohol and 53.73 volumes of water, owing to volume contraction. Ordinary alcohol of 95% strength is thus 190-proof alcohol, and pure anhydrous alcohol is 200-proof. It is interesting to observe that 100-proof alcohol is about the lower limit of burning for alcohol dilutions by direct ignition at ordinary temperatures. A *wine gallon* is a measure of volume (231 cu in.) of any proof.

authorities. Such special formulas are limited to certain designated processes and are manufactured, stored, and used under bond, to ensure such specially denatured alcohols from unlawful consumption. However, the 40 approved special formulas under their authorized uses enter into an exceedingly broad section of the entire industrial life of the nation.[1] Typical specially denatured formulas[2] are

To every 100 gal of ethyl alcohol, add for the designated number:
No. 1. Five gallons approved wood alcohol. Withdrawals for
Authorized uses: plastics, dehydrations, explosives, food products, chemicals, etc.
No. 28. One-half gallon benzene or one-half gallon rubber hydrocarbon solvent.
Authorized uses: plastics, dehydrations, explosives, food products, chemicals, etc.
No. 29. One gal of 100% acetaldehyde or other approved denaturant. Withdrawals for
Authorized uses: manufacturing acetaldehyde, acetic acid, esters, ethers, etc.

In industrial nomenclature *alcohol* means ethyl alcohol or ethanol with the formula C_2H_5OH. It is sold by the gallon, which weights 6.794 lb and contains 95% C_2H_5OH and 5% H_2O both by volume and at 15.56 C.[3] No distinction is made as to the source of the alcohol, whether from fermentation or from synthesis.

USES AND ECONOMICS Tax-paid pure alcohol is used only for medicinal, pharmaceutical, flavoring, and beverage purposes. The large consumption and the wide field of industrial application have arisen only since the availability of the low-priced tax-free denatured alcohols. Completely denatured alcohol is consumed chiefly as an antifreeze. The trend has been toward the use of specially denatured alcohols for industrial applications. Alcohol is second only to water in solvent value, and is employed in nearly all industries. In addition, it is the raw material for making hundreds of chemicals. Most important of these are acetaldehyde, ethyl acetate, acetic acid, ethylene dibromide, glycols, and ethyl chloride. During World War II, when tremendous quantities of butadiene and styrene were needed for the synthetic-rubber program, alcohol was used as a supplemental raw material for butadiene, although petroleum is the cheaper raw material. In fact, in 1945, 75% of the specially denatured alcohol entered into synthetic-rubber manufacture.

In petroleum-poor countries it is economical to mix alcohol (frequently absolute) in with the gasoline in order to conserve the petroleum products. For such mixtures, if the alcohol is not anhydrous, a blending agent is needed. These procedures have been carried out quite extensively in Europe and in some tropical sugar-growing countries, where from 10 to 20% alcohol may be in the motor fuel, the higher amount having been employed in Sweden for many years. Similar proposals have been made for the United States, and even tried in localized areas, but were uneconomical.

The cost of alcohol is largely that of the raw material, although steam, overhead, labor, and other factors vary as to location. Raw materials from which ethyl alcohol may be made fall into five general classifications: (1) hydrocarbon gases, (2) starchy materials (cereal grains, potatoes), (3) fruit, (4) cellulosic materials (wood, agricultural residues, and waste sulfite liquors), and (5) saccharine materials (molasses from sugar beets and sugar

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[1] Withdrawals of specially denatured alcohol in 1965 amounted to 308.5 million wine gallons, with only 2.2 million wine gallon of completely denatured alcohol.

[2] Formulas for Denatured Alcohol, U.S. Revenue Service, Part 12 of Title 26, Federal Regulations, 1961.

[3] This corresponds to 92.423% of ethyl alcohol by weight. However, when alcohol percentage strength is given, it refers to percentage by volume.

TABLE 31.2 *Ethyl Alcohol Production by Type of Raw Material (In thousands of gallons of alcohol and spirits of 190 or more proof, fiscal year ending June 30)*

Raw material	*1965*	*1964*	*1963*	*1959*	*1917*
Ethyl sulfate	447,596	442,078	408,867	362,151	133,306
Molasses	4,234	1,282	1,445	39,467	54,159
Ethylene gas	117,633	98,229	88,657	75,463	
Products used in redistillation	33,101	49,506	43,711	8,393	49,546
Grain and grain products	80,223	83,343	90,000	7,460	39,742
Sulfite liquors	7,050	7,286	5,824	6,254	4,380
Cellulose pulp, chemical, and crude alcohol mixtures	2,076	2,214	1,681	2,057	2,422
Fruit	21,728	29,843	26,049	494	220
Whey	266				
Potatoes	20	22	41	970	15,146
Marshmallows	5				
Total alcohol produced	713,932	713,803	666,336	502,712	28,581

Source: U.S. Treasury, Internal Revenue. Starting with 1961 some beverage alcohol is included under "grain."

cane). See Table 31.2. Molasses contains from 50 to 55% of fermentable sugar, consisting mainly of 70% sucrose and 30% invert (glucose-fructose mixture) sugar.

The economics of the situation have changed until fermentation is occupying a place of minor importance as a source of *industrial* alcohol. The year 1950 was the first year that fermentation accounted for less than 50% of the alcohol produced, the greater part being synthetically derived. The beverage laws specify the use of grain alcohol in certain beverages (whisky), and custom demands it for some tax-paid solvent uses. Thus a demand is created for this higher-priced grain alcohol, which means that lower-priced synthetics under these conditions will not entirely displace fermentation alcohol.

MANUFACTURE OF INDUSTRIAL ALCOHOL

RAW MATERIALS The manufacture of alcohol from ethylene or other synthetic manufacturing procedures, now the most important source, is discussed in Chap. 38 and illustrated by the flowchart of Fig. 38.9. Alcohol from cellulosic materials, wood, wood wastes, and sulfite liquors, is considered in Chap. 32, principally under *wood saccharification*, where yields and references are given. This last is not competitive except under special conditions, largely because of the cost of converting the cellulosic material to fermentable sugars.

REACTIONS The principal reaction in alcohol fermentation is

Equation of inversion:[1]

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{d\text{-Glucose}}{C_6H_{12}O_6} + \underset{d\text{-Fructose}}{C_6H_{12}O_6}$$

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[1] In commercial parlance, reducing, or invert, sugars are fermented and include the scientific *d*-glucose and *d*-fructose. The product sold commercially as glucose is usually a sirup of *d*-glucose with some dextrin and maltose, whereas dextrose USP is *d*-glucose.

Equations of fermentation:[1]

$$\underset{\text{Monosaccharide}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2 \qquad \Delta H = -31.2 \text{ kcal}, \Delta F = -51.4 \text{ kcal} \tag{1}$$

Toward the end of a fermentation, the acidity and glycerin increase. Neuberg's third equation may account for this.

$$\underset{\text{Monosaccharide}}{2C_6H_{12}O_6} + H_2O \longrightarrow \underset{\text{Alcohol}}{C_2H_5OH} + \underset{\substack{\text{Acetic}\\ \text{acid}}}{CH_3COOH} + 2CO_2 + \underset{\text{Glycerin}}{2C_3H_8O_3} \tag{2}$$

A small amount of glycerin is always found in alcohol fermentations.

ENERGY REQUIREMENTS, UNIT OPERATIONS, CHEMICAL CONVERSIONS The shipment of raw material may involve tank-car movement of molasses to the Puerto Rican shore, steamer to an American port, and barge or tank-train transshipment to a plant, if inland. The plant procedures require steam heating for distillation, power for pumping, and water for condensation, and occasionally for cooling, during the exothermic fermentation. The heat evolved by this fermentation reaction calculates to 88,940,000 kg-cal, or 353 million Btu per 1,000 gal of 95% alcohol. Its evolution usually takes about 60 hr.

The manufacture of alcohol, as presented in Fig. 31.1, can be broken down into the following principal *chemical conversions* (Ch) and *unit operations* (Op). The main steps in the competitive manufacture of alcohol from petroleum cracking (cf. Fig. 38.9) are shown in parallel comparison.

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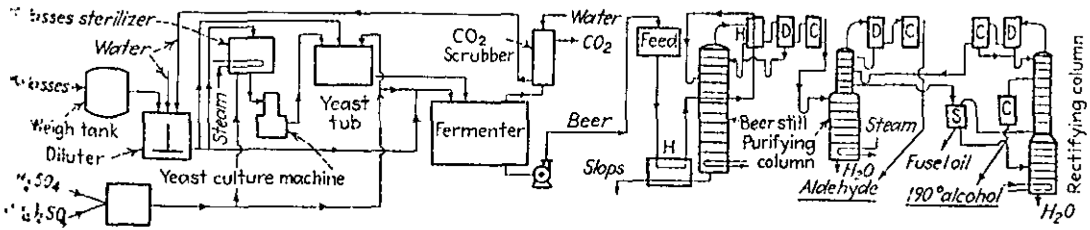
[1] This is the classic Gay-Lussac equation for alcohol formation. It is the principal equation in acid or low-pH medium. When growing yeast for sale as such or for inoculation, usually with some air blown in, the yield of alcohol is lower, it being partly changed to CO_2 and H_2O. This fermentation, however, like so very many industrial reactions, is very much more involved than these simple reactions indicate. Probably the first step is a phosphate hexose ester formation, followed by a split in the 6-carbon chain. Cf. Michaelis, Chemistry of Alcoholic Fermentation, *I&EC,* 27, 1037 (1935). The fusel oil (mixed amyl alcohols with some propyl, butyl, and hexyl alcohols and esters), amounting to 3 to 11 parts per 1,000 of alcohol, obtained from yeast fermentations, is held to be furnished by the protein materials in the *mash* fermented. Cf. Prescott and Dunn, Industrial Microbiology, 3d ed., chap. 4, McGraw-Hill, 1959; Underkofler (ed.), Commercial Fermentations, Chemical Publishing, 1952.



Key C= Condenser D= Dephlegmator H= Heat exchanger S= Separator

Molasses	2.5 gal.	Process water	10 gal.	Per gal. 190 proof alcohol
H_2SO_4 (60° Bé.)	0.17 lb.	Cooling water	42 gal.	
$(NH_4)_2SO_4$	0.015 lb.	Electricity	0.11 kw-hr.	
Steam	50 lb.	Direct labor	0.01 man-hr.	

Fig. 31.1 Flowchart for industrial alcohol.

Fermentation alcohol

Transportation of molasses or corn (Op)
Storage of molasses or corn (Op)
Grinding, etc., of corn (Op)
Hydrolysis by heating of cornmeal with malt or acid to make mash (Ch)
Growth of inoculating cultures (Ch)
Fermentation of diluted inverted molasses or of corn mash (Ch)
Distillation of alcohol from "beer" (Op)
Rectification and purification of alcohol (Op)
Recovery of by-products, e.g., CO_2, feed, potash salts (Op)

Alcohol from ethylene[1]

Liquefaction of the petroleum gases contain ethylene (Op)
Rectification to produce pure ethylene and pu ethane (Op)
Dehydrogenation of ethane to ethylene (Ch)
Esterification of strong sulfuric acid by ethyle (Ch)
Hydrolysis of diluted ester to alcohol and dilu sulfuric acid (Ch)
Distillation of alcohol from acid (Op)
Rectification and purification of alcohol (Op)
Concentration of diluted sulfuric acid to str acid (Op)
Recovery of by-products, e.g., ether (Op)

MAKING OF INDUSTRIAL ALCOHOL The flowchart in Fig. 31.1 shows the various operations and conversions involved in changing molasses into salable alcohol. Molasses, because of the strong concentration of sugar, does not support direct yeast fermentation. It must be diluted first to a concentration of up to 17% sugars. This is called the *mash*, and represents the carbohydrate ready for yeast inoculation. It is pumped to a large steel fermentor (60,000 to 500,000 gal), closed, in modern plants, to collect the carbon dioxide evolved and to afford easier conditions for cleaning and sterilizing. An ammonium salt and sulfuric acid are added, the one to furnish a nutritive constituent deficient in molasses, and the other the right environmental pH (4.0 to 5.0) to facilitate the activity of the selected yeast and to suppress the multiplication of wild yeasts or bacteria. Magnesium sulfate is also added, when deficient, as is a small amount of a phosphate (generally as superphosphate)

In the meanwhile a charge of the selected yeast (about 5% of the total volume) has been growing in the yeast tub. All this is under exact laboratory supervision, including the selection of the inoculating yeast strain, the sterilization of the diluted molasses, the addition of the nutrients, the pH, the temperature (76 F), and finally the cleaning and sterilizing of the yeast culture machine in readiness for the next batch. The bacteriologists have been able to cultivate a strain of yeast that thrives under these acid conditions, whereas wild yeast and bacteria do not. As the reaction study indicates, the fermentation is exothermic, and so cooling by outside sprays is frequently used; hence one advantage of the steel fermentor. Although the most favorable temperature varies, it is usually about 70 F for starting and under 100 F at the end. Four days are allowed by government regulations for a fermentation cycle, though usually 36 to 50 hr are used. As alcohol is formed by yeast only from monosaccharides, it is necessary to split the sucrose, $C_{12}H_{22}O_{11}$, into *d*-glucose and *d*-fructose.[3] In alcohol fermentation by yeast, this microorganism furnishes an organic catalyst, or enzyme, known as *invertase*, which effects this hydrolysis. The yeast also produces another and more important enzyme, *zymase*, which changes the monosaccharides into alcohol and carbon dioxide. The flowsheet of Fig. 7.2 outlines the procedure for purification of the carbon dioxide from fermentation. Such recovery is pre

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[1] About one-fifth of the synthetic alcohol from ethylene is made by acidic catalytic hydration at high temperat

[2] Indeed, strong sugar sirup is a *preservative;* witness the preserving of fruits with it.

[3] An equimolecular mixture of these is known as *invert* sugar, and results by the action of heat, acids, or enzym

ticed from a number of different fermentations—industrial alcohol, whisky, and butanol-acetone.

When *starchy materials* are used for industrial alcohol, they may be converted to maltose, a disaccharide. This can be done with either malt or various mold processes. The *malt process*, except for emergency periods, is too expensive for industrial alcohol. *Fungal amylase*, an enzymatic material produced by the fermentation of *Aspergillus niger*, has been found to be an economical[1] replacement of malt for industrial alcohol. In addition, fungal amylase cannot replace barley malt for beverage production, since the flavor is not the same and because of Federal regulations. During World War II, grain processing changed from batch to continuous cooking and hydrolyzing processes.[2] Two types of such cookers were used commercially: a pipeline cooker, operated at 350 F with a holding time of 1 to 2 min, and a vertical tower, embodying a lower temperature and longer holding time.

The liquor in the fermentors, after the action is finished, is called a *beer*.[3] The alcohol is separated by *distillation*.[4] In such fermentation as pictured in Fig. 31.1, the beer, containing from 6.5 up to 11% alcohol by volume, is pumped to the upper sections of the beer still, after passing several heat exchangers. As the beer passes down the beer column, it gradually loses its lighter-boiling constituents. The liquid discharged from the bottom of the still through a heat exchanger is known as *slop* or *stillage*.[5] It carries proteins, some residual sugars, and, in some instances, vitamin products, so that it is frequently evaporated and used as a constituent of animal feed. The overhead containing alcohol, some water, and the aldehydes passes through a heat exchanger to the partial condenser, or dephlegmator, which condenses sufficient of the vapors to afford a reflux and also to strengthen the vapors that do pass through to the condenser, where about 50% alcohol, containing the volatiles or aldehydes, is condensed. This condensate, frequently known as the *high wines*, is conducted into the aldehyde, or heads, column, from which the low-boiling impurities, or aldehydes, are separated as an overhead. The effluent liquor from part way down the aldehyde column flows into the rectifying column.

In this third column the alcohol is brought to strength and finally purified in the following manner: the overhead going through a dephlegmator is partly condensed to keep the stronger alcohol in this column and to provide reflux for the upper plates. The more volatile products, which may still contain a trace of aldehydes and of course some alcohol, are totally condensed and carried back to the upper part of the aldehyde still. Near the top of the column 95 to 95.6% alcohol is taken off through a condenser for storage and sale. Farther down the column, the higher-boiling fusel oils are run off through a cooler and separator to a special still, where they are rectified from any alcohol they may carry, before being sold as an impure amyl alcohol for solvent purposes. The bottom of this rectifying column discharges water.

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[1] Grain Alcohol without Malt, *CW*, 68 (3), 19 (1951); Methods and Costs of Producing Alcohol from Grain by the Fungal Amylase Process on a Commercial Process, *USDA Tech. Bull.* 1024.

[2] Stark *et al.*, Wheat as a Raw Material for Alcohol Production, *I&EC*, 35, 133 (1943); Continuous Cooking of Cereal Grains, *Chem. & Met. Eng.*, 51 (10), 142 (1944) (pictured flowchart); Recent Advances in Fermentation, *CE*, 54 (12), 141 (1947).

[3] This is a general term applied to the result of any such fermentation, whether it results finally in industrial alcohol or the beverage beer, or whisky, or butanol and acetone.

[4] ECT, 2d ed., vol. 1, pp. 501-537; Bosworth, Alcohol Rectification, *CEP*, 61 (9), 82 (1965).

[5] Reich, Molasses Stillage, *I&EC*, 37, 534 (1945).

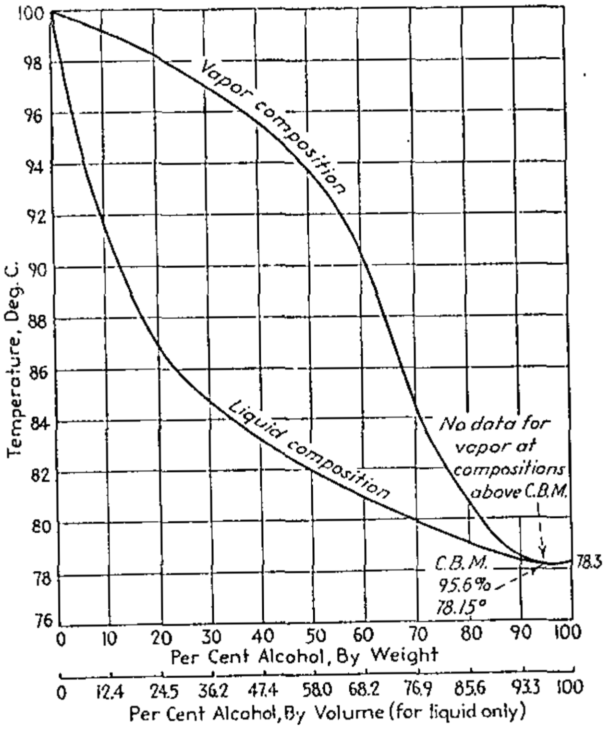

Fig. 31.2 Temperature versus composition of vapor and liquid for alcohol-water at 760 mm.

Alcohol-water mixtures are rectified to increase the strength of the alcohol component by virtue of the composition of the vapors being stronger in the more volatile constituent than the liquid from which these vapors arise. This is shown quantitatively by the curves of Fig. 31.2, where the composition of the vapor in equilibrium with the liquid is on a horizontal line. However, alcohol cannot be made stronger by rectification than 95.6%, because, as can be seen from Fig. 31.2, water forms a binary constant boiling mixture of this composition which boils slightly lower than absolute, or anhydrous, alcohol. The principles shown here are the basis of the strengthening of the more volatile constituent of any liquid mixture by distillation.

ABSOLUTE, OR ANHYDROUS, ALCOHOL[1]

Anhydrous alcohol was made by absorbing the 4 or 5% of water present in 95 to 96% industrial alcohol, using quicklime, with subsequent distillation. This process was expensive, and although it produced a very high quality of anhydrous alcohol, it has now been superseded largely by improved chemical-engineering unit operations of distillation and extraction involving a third component. This has led to lower cost of dehydrating operations, mostly of a continuous nature, using preferably all liquids or solutions, and has

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[1] This is practically 100% ethyl alcohol, frequently known as *absolute* alcohol, but since the absence of water is more notable than that of other impurities, the term *anhydrous* alcohol is preferred by some.

resulted in reducing the price of anhydrous alcohol to a figure only slightly in excess of the usual selling value of the alcohol contents.

The water in 95% alcohol is removed technically by either of two principal methods: (1) Dehydration by *distillation with a third component,*[1] which forms a minimum constant boiling mixture in the system, boiling at a lower temperature than the 95% alcohol (78.15 C) or the water. Here (*a*) the minimum is a binary one, of which water-ethyl ether is an example,[2] or (*b*) the minimum is a ternary one, of which alcohol-water-benzene is an example. In such instances anhydrous alcohol is obtained at the bottom of the distilling column, because its vapor pressure is relatively lower than that of the constant boiling mixture removing the water. (2) Dehydration by *countercurrent extraction,*[3] usually also in a continuous column, with a third component which depresses the vapor pressure of water more than it depresses the vapor pressure of alcohol, e.g., glycerol, ethylene glycol, glycerol or glycol with dissolved salts, and molten eutectic mixture of Na and K acetates. Anhydrous alcohol comes out at the top of the extraction column.[4]

The basic principle of the process using benzene as a withdrawing agent is illustrated[5] by Fig. 31.3. There are three binary minimum constant boiling mixtures (cbm) in the

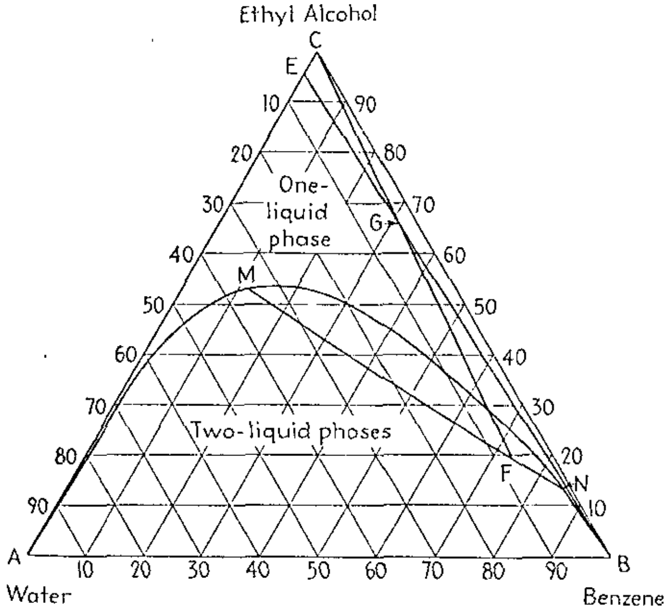

Fig. 31.3 Ternary diagram of liquid system water-alcohol-benzene.

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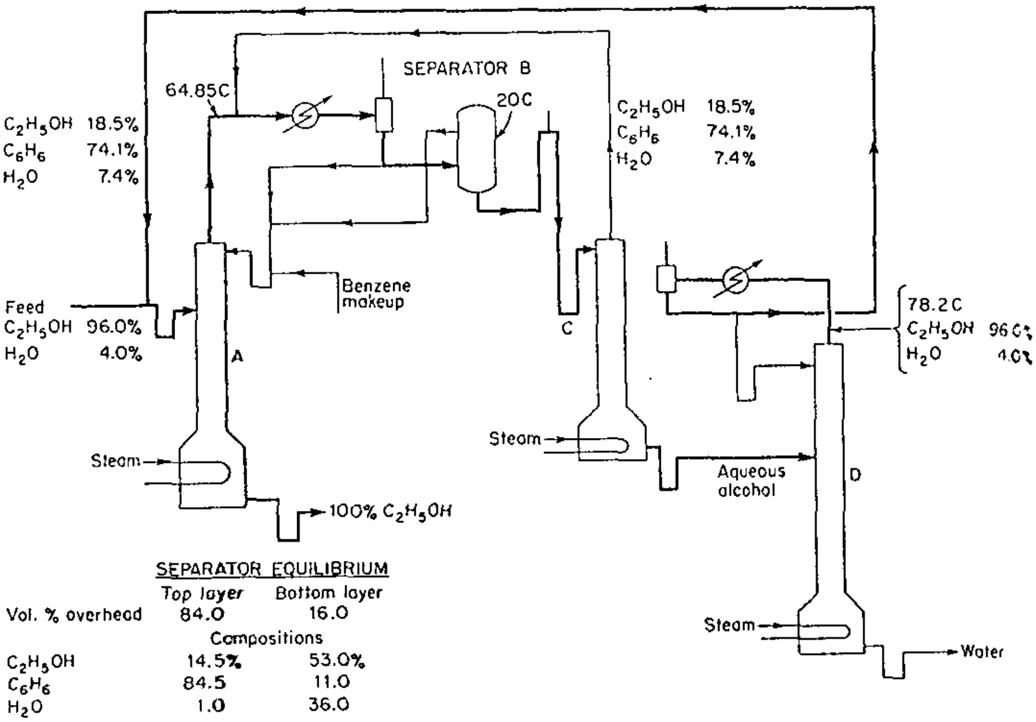
[1] This third component is frequently called a *dehydrating,* or *withdrawing, agent,* or simply an *entrainer.* See ECT, 2d ed., vol. 2, pp. 839–859, 1963. References.

[2] Othmer and Wentworth, Absolute Alcohol, *I&EC,* **32,** 1588–1593 (1940). Here the water is removed overhead by ether, the system being under 100 lb pressure.

[3] Othmer and Trueger, Recovery of Acetone and Ethanol by Solvent Extraction, *Trans. AIChE,* **37,** 597–619 (1941).

[4] The use of a solid dehydrating agent, such as quicklime or calcium sulfate, may be looked upon as an extreme case of this method, though usually run in a discontinuous manner because of the solid involved.

[5] A somewhat similar procedure is the ether pressure system of Othmer and Wentworth, *op. cit.*



SEPARATOR EQUILIBRIUM

	Top layer	Bottom layer
Vol. % overhead	84.0	16.0
	Compositions	
C_2H_5OH	14.5%	53.0%
C_6H_6	84.5	11.0
H_2O	1.0	36.0

Fig. 31.4 Dehydration of 96% ethanol to absolute alcohol by azeotropic distillation with benzene at 1 atm. 96% alcohol is fed to column *A*. The ternary azeotrope is taken overhead in this column, and absolute alcohol is obtained as bottoms product. The overhead vapors are condensed and passed to separator (decanter) *B*, in which two liquid layers form. The upper layer, rich in benzene, is returned to column *A* as reflux, and the lower layer is fed to column *C*, which produces the ternary azeotrope as the overhead product and benzene-free aqueous alcohol as the bottoms product. This latter product is fed to column *D*, which produces by ordinary distillation an overhead product 96% alcohol and a bottoms product nearly pure water. The overhead from column *D* is recycled to column *A* for removal of the water. The benzene is recycled continuously in this system, and it is necessary only to make up the benzene losses from the system. This withdrawing agent is used over and over again with a loss that should not exceed 0.05% on the volume of the anhydrous alcohol produced. [*Perry, pp. 13-45, 13-50; CE,* 67 *(10), 129 (1960).*]

system, two homogeneous ones and one heterogeneous one (between water and benzene), and a ternary minimum constant boiling mixture which is the lowest-boiling composition in the system, boiling at 64.85 C. In Fig. 31.3 the composition of the ternary minimum constant boiling mixture is represented by point *F*. In order that the removal of the charge from the starting mixture may leave anhydrous alcohol in the still, the starting composition must lie on the straight line *CF*. If the starting mixture is to be made up by adding benzene to 95% alcohol, the starting composition must also lie on the line *EB*. Therefore the intersection *G* represents the starting composition. If enough benzene is added to 95% alcohol to bring the total composition to point *G*, continuous distillation gives the ternary constant boiling mixture (bp 64.85 C) at the top of the column and absolute alcohol (bp 78.3 C) at the bottom of the column in a simple distillation.

An important[1] feature of the process is the separation of the condensate into two

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[1] Guinot and Clark. Azeotropic Distillation in Industry, *Trans. AIChE (London)*, 16, 189 (1938).

liquid layers, represented in Fig. 31.3 by points *M* and *N*. The ratio of the top layer *N* to the bottom layer *M* is equal to *MF*/*FN*, or 84:16. The compositions involved are shown on Fig. 31.4, which also illustrates how this process functions. These same principles of distillation in multicomponent systems, involving constant boiling mixtures, are used for dehydrating other organic liquids, such as propyl alcohol, and for removing the water formed in sulfonations (benzene-sulfonic acid) and esterifications (ethyl acetate).[1] The fundamentals of distillation are here presented because of the extensive data on alcohol that are available.

BEERS, WINES, AND LIQUORS

The making of fermented beverages was discovered by primitive man, and has been practiced as an art for thousands of years. Within the past century and a half this has evolved into a highly developed science. As Muspratt writes, "There is no department of the arts and manufactures where chemistry has exerted a more decided influence than in brewing." But E. A. Siebel adds to this, "A modern brewer has to be an engineer, a chemist, and a bacteriologist." In common with other food industries, the factors of taste, odor, and, almost, of individual preference exist, to force the manufacturer to exert the greatest skill and experience in producing palatable beverages of great variety. In the last analysis, the criterion of quality, with all the refinements of modern science, still lies in the human sensory organs of taste, smell, and sight.

USES AND ECONOMICS As Table 31.3 indicates, many millions of barrels of alcoholic beverages are manufactured in the United States each year.

RAW MATERIALS Grains and fruits supplying carbohydrates are the basic raw materials. The variety of grains and fruits employed is wide, changing from country to country or from beverage to beverage. Russia ferments potatoes and by distillation obtains vodka; similar treatment of the sap of the maguey in Mexico yields pulque; but the world's chief raw materials for fermentations are the cereals, corn, barley, and rice, together with the grape.

MAKING OF BEER[2] Beer and allied products are beverages of low alcoholic content (2 to 7%) made by brewing various cereals with hops, usually added to impart a more or less bitter taste and to control the fermentation that follows. The cereals employed are barley, malted to develop the necessary enzymes and the desired flavor, as well as malt adjuncts: flaked rice, oats, and corn, with wheat used in Germany and rice and millet in

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[1] Consult Perry, sec. 13, on distillation, for a rigorous and fundamental treatment of this important unit operation.

[2] Shearon and Weissler, Brewing, *I&EC*, **43**, 1262 (1951) (many excellent pictures, tables, and diagrams); ECT, 2d ed., vol. 3, p. 297, 1964.

TABLE 31.3 ***U.S. Production of Alcoholic Beverages, Fiscal Years 1939, 1950, 1963–1965 (In thousands)***

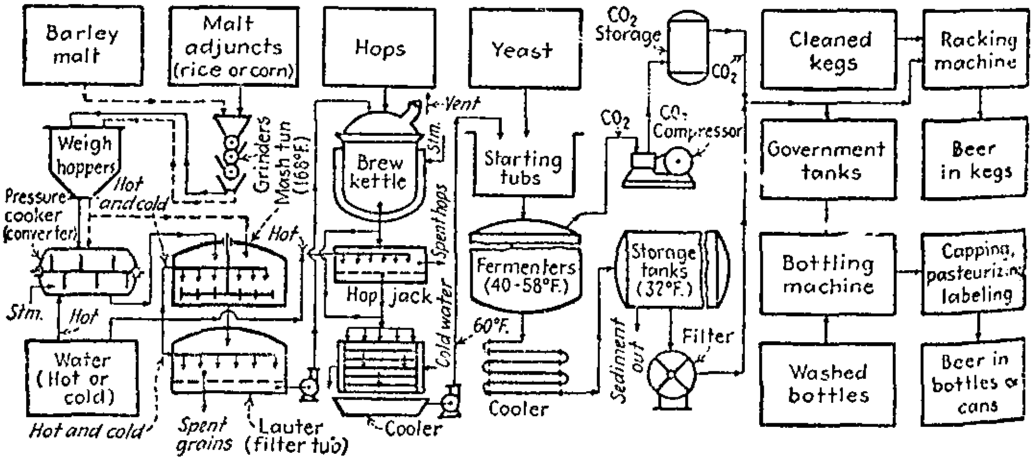
Beverage	*1965*	*1964*	*1963*	*1950*	*1939*
Still, wine gal	197,257	200,572	191,220	297,857	231,986
Sparkling, wine gal	6,358	5,305	4,485	21,225	6,634
Rectified, proof gal	92,923	88,033	87,617	107,951	43,401
Fermented, bbl	108,015	103,018	97,961	98,807	53,571
Cereal, bbl	73	57	35	45	63

Source: U.S. Treasury, Internal Revenue. *Note:* bbl contains 31 gal.

China. Brewing sugars and sirups (corn sugar, or glucose) and yeast complete the raw materials. For beer the most important cereal is barley, which is converted into malt by partial germination.[1]

The barley is steeped in cold water and spread out on floors or in special compartments and regularly turned over for from 5 to 8 days, the layers being gradually thinned as the germination proceeds. At the proper time, when the enzymes are formed, the growth is arrested by heat. During the growth, oxygen is absorbed, carbon dioxide given off, and the enzyme *diastase* formed. This latter is the biological catalyst that changes the dissolved starch into the disaccharide maltose which, after transformation into the monosaccharide glucose by the *maltase* enzyme, is directly fermentable by yeast.

The flowchart for beer in Fig. 31.5 may be divided into three groups of procedures: (1) brewing of the mash through to the cooled hopped wort, (2) fermentation, and (3) storage, finishing, and packaging for market. *Mashing* is the extraction of the valuable constituents of malt, malt adjuncts, and sugars by macerating the ground materials with 7.5 to 9 bbl of water per 1,000 lb of materials listed in Fig. 31.5 and water-treated to prevent too high pH, which would tend to make a dark beer. In the pressure cooker the insoluble starch is converted into liquefied starch, and the soluble malt starch into dextrin and malt sugars. The resulting boiling cooker mash, mixed with the rest of the malt in the mash tun, raising the temperature to 168 F, is used to prepare the brewers' *wort*.[2]



Brewer's malt	35-38 lb.
Malt adjuncts	12-14 lb.
Hops	½-1¼ lb.
Yeast	¾-1 lb.

Brewery labor	\$0.50-\$1.50	Per U.S. barrel (31 gal.) of beer
Power and steam	0.50-0.70	
Bottling costs (labor labels, alkali, etc.)	1.50-2.50	

Fig. 31.5 Flowchart for manufacture of beer.

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[1] Brewing of Lager Beer, *Chem. & Met. Eng.*, **49** (7), 112 (1942) (pictured flowchart); cf. ECT, 2d ed., vol. 2, pp. 384–413; Staff Industry Report, Beer, *I&EC*, **43**, 1264 (1951); Chopey, What's Doing in Beer Brewing?, *CE*, **69** (13), 94 (1962) (process flowchart with pictures); continuous-flow beer making is now practiced (1964) by Carling in Fort Worth, Tex.; Continuous Beermaking, *CE*, **72** (1), 18 (1965).

[2] The wort is the liquid resulting from the mashing process, i.e., the extracting and solubilizing of the malt and malt adjuncts. Wort composition varies from 17 to 24% solids by weight for the first wort to approximately 1% solids for the last wort removed by the sparge water.

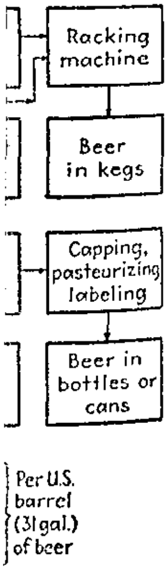
This is carried out in the mash tun. After all the required ingredients have been dissolved from the brewing materials, the entire mash is run from the mash tun to filter presses or the lauter or straining tub, where the wort is separated from the insoluble spent grains through a slotted false bottom and run into the copper wort cooker. For complete recovery of all substances in solution, a spray of decarbonated water at 165 F is rained through the grains. This is called *sparging*.

The wort is cooked for approximately 3 hr, during two of which it is in contact with hops. The purpose of boiling is to concentrate the wort to the desired strength, to sterilize it (15 min) and destroy all the enzymes, to coagulate certain proteins by heat (180 F), to modify the malty smell of the wort, and to extract the hop resins' tannin and aroma from the hops, which are added during the cooking process. At the end of the 3 hr the spent hops are separated from the boiling wort very quickly through a false bottom in the hop jack or strainer underneath the copper cooker. Since the spent hops retain 3 bbl of wort per 100 lb of hops, they should also be sparged. The wort is then ready to be cooled.

The cooling step is not only to reduce the temperature, but also to allow the wort to absorb enough air to facilitate the start of the fermentation. In addition, the protein and hop resins are precipitated. The hot wort may be first cooled to about 150 to 160 F in a large shallow cooler, where certain of the resins precipitate. The wort is then run over the horizontal, brine-cooled copper tubes of the open Baudelot cooler or through a shell and tube heat exchanger,[1] where aeration also takes place. Slight concentration, due to evaporation, occurs. This operation is performed under controlled conditions to prevent contamination by *wild* yeasts. Frequently, sterilized air is used.

The cooled wort is mixed with selected yeasts in the line leading to the starting tubs, between $\frac{3}{4}$ and 1 lb of yeast being used per barrel of beer. The initial *fermentation* temperature is 40 to 43 F, but as the fermentation proceeds, the temperature rises to 58 F. This is easily explained by the fact that the conversion of the sugar to CO_2 and ethyl alcohol by the enzymes of the yeast generates 280 Btu/lb of maltose converted. The temperature is partly controlled by attemperators inserted in the fermentors. The mixture is skimmed to remove the foreign substances that the evolved carbon dioxide brings to the top. Thus it is quite evident that a steady evolution of gas is necessary to cleanse the beer properly. The CO_2 evolved is collected by using closed fermentors and stored under 250 lb pressure for subsequent use in carbonating beer.

The yeast gradually settles to the bottom of the tub, so that at the end of 7 to 10 days the fermented beer is ready to be vatted. The liquid is very opalescent in appearance, under a cover of foam. As the beer leaves the fermenting cellar, it contains in suspension hop resins, insoluble nitrogenous substances, and a fair amount of yeast. The beer is cooled to 32 F, and stored in the cellar for 3 to 6 weeks at this temperature. During this period, clarification, separation, and precipitation of hard resins and improvement in palatability (mellowing) occur. At the end of the period the beer is carbonated[2] and pumped through a pulp filter with or without such non-taste-imparting filter aids as asbestos fiber. In the United States, public demand favors a brilliant beverage. As a result, the beer is sometimes refiltered through cotton pulp, keeping carbon dioxide on the entire system. About 97 bbl of beer is produced per 100 bbl of wort in the starting tubs. After *bottling, the beer is pasteurized at* 140 F.



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[1] Cf. Chopey, *op. cit.*

[2] The carbon dioxide should be kept free from air, which would interfere with the stability and quality of the beer. The gas is pumped in close to 32 F and amounts to between 0.36 and 0.45% of the weight of the beer.

MAKING OF WINE Wine has been made for several thousand years by fermentation of the juice of the grape. Like other fermentations, many of the primitive procedures have been supplanted by improved science and engineering, to reduce costs and to make more uniform products. But now, as always, the quality of the product is largely related to grape, soil, and sun, resulting in variation in flavor, bouquet, and aroma. The color depends largely upon the nature of the grapes and whether the skins are pressed out before fermentation. Wines are classified as natural (alcohol 7 to 14%), fortified (alcohol 14 to 30%), sweet or dry, still or sparkling. The fortified wines have alcohol or brandy added. In the sweet wines some of the sugar remains.

For the manufacture of dry red wine, red or black grapes are necessary. The grapes are run through a crusher, which macerates them but does not crush the seeds, and also removes part of the stems. The resulting pulp, or *must,* is pumped into 3,000- to 10,000-gal tanks,[1] where sulfurous acid[2] is added to check the growth of wild yeast. An active culture of selected and cultivated yeast equal to 3 to 5% of the volume of juice is added. During fermentation, the temperature rises, so that cooling coils are necessary to maintain a temperature below 85 F. The CO_2 evolved carries the stems and seeds to the top, which is partly prevented by a grating floated in the vat. This allows an extraction of the color and the tannin from the skins and seeds. When the fermentation slows up, the juice is pumped out of the bottom of the vat, back over the top. The wine is finally run into closed tanks in the storage cellar, where, during a period of 2 or 3 weeks, the yeast ferments the remainder of the sugar. The wine is given a cellar treatment to clear it, improve the taste, and decrease the time of aging. During this treatment the wine is first allowed to remain quiet for 6 weeks to remove part of the matter in suspension, then racked for clarification.[3] Bentonite, or other diatomaceous earth, may be used for clearing, 2 to 16 lb being stirred into every 1,000 gal of wine. An insoluble precipitate with the tannin is also formed. Extra tannin may also be added, and the wine racked and filtered through diatomaceous earth, asbestos, or paper pulp. The wine is corrected to commercial standards by blending it with other wines and by the addition of sugar, acids, or tannins. It is standard procedure to chill some wines for removal of argols or crude potassium acid tartrate, which constitute the commercial source of tartaric acid and its compounds. This treatment also gives a more stable finished wine. By quick-aging methods it is possible to put out a good sweet wine in 4 months. These methods include pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation, and aeration. The wine may be held at about freezing for 3 weeks to a month, and a small amount of oxygen gas bubbled in. Then the wine is racked, clarified, and further filtered in the usual manner.

DISTILLED SPIRITS Various fermented products, upon distillation and aging, yield the distilled liquors. Figure 31.6 shows the flowchart for whisky and gin, and Table 31.4 presents statistics. Brandy is distilled from wine or from the *marc,* which is the pulp left

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[1] In many of the modern American wineries these tanks are even larger and are constructed of concrete.

[2] Potassium or sodium metabisulfite and/or sodium bisulfite may also be used.

[3] During this and the following period the new wine undergoes a complicated series of reactions, resulting in the removal of undesired constituents and the development of the aroma, bouquet, and taste. Oxidation takes place, as well as precipitation of proteins and argols and esterification of the acids by alcohols. Certain modifications of this process are presented by Havinghorst, Winers Keep Age-old Process Current, *CE,* 68, 76 (1961) (process flowchart).

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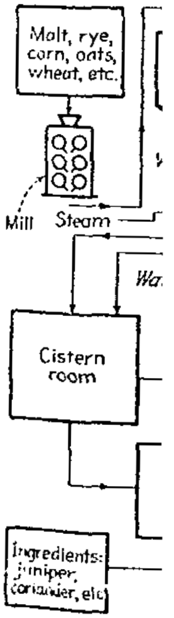

Fig. 31.6 F

by racking or straining. By making a beer[1] from a grain mixture containing at least 51% of corn and *distilling and aging it, bourbon* whisky is yielded. Similarly, rye whisky must have started with 51% of rye in the grain to be mashed and fermented. By inspecting the flowchart of Fig. 31.6 in the light of Figs. [illegible] and 31.5, and the description accompanying them, the procedures of Fig. 31.6 for distilled liquors will be clear. The equipment,[2] up to the stills, in modern liquor plants is of steel, with the stills of copper. By law, *the aging of bourbon or rye whisky of* [illegible] age must take place in charred new white-oak barrels of approximately 50 gal. They are kept in bonded warehouses at 65 to 85 F and at a preferred humidity of 65 to [illegible] for 1 to 5 years, usually. During this time an evaporation of the contents takes place, largely through the ends of the barrel staves. By reason of a more rapid capillary flow and osmosis of the smaller water molecules *in comparison with alcohol molecules,* an increase in percentage of alcohol is found in the barrel contents. The government shrinkage allowance is approximately 8% the first year, 4% the second year, 4% the third year, and 3% the fourth year. If the shrinkages are exceeded (and this is often the case), the manufacturer must pay a *tax on the* excess, but with the best cooperages under the best conditions, these allowances can just be met. *The distillate from the spirit* still is over 160 proof, and is subsequently diluted

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[1] The yeast in this fermentation is grown in the presence of [illegible] acid to ensure proper strain and to secure the desired quality of the product (whisky).

[2] Owen, Modern Distillery Design, *Sugar,* **37** (3), 2[illegible] (1942); *Chem. & Met. Eng.,* **49** (11), 126 (1942) (pictured flowchart of a distillery); Stallings *et al.,* [illegible] Engineering Developments in a Grain Distillery, *AIChE,* 38, 791 (1942).

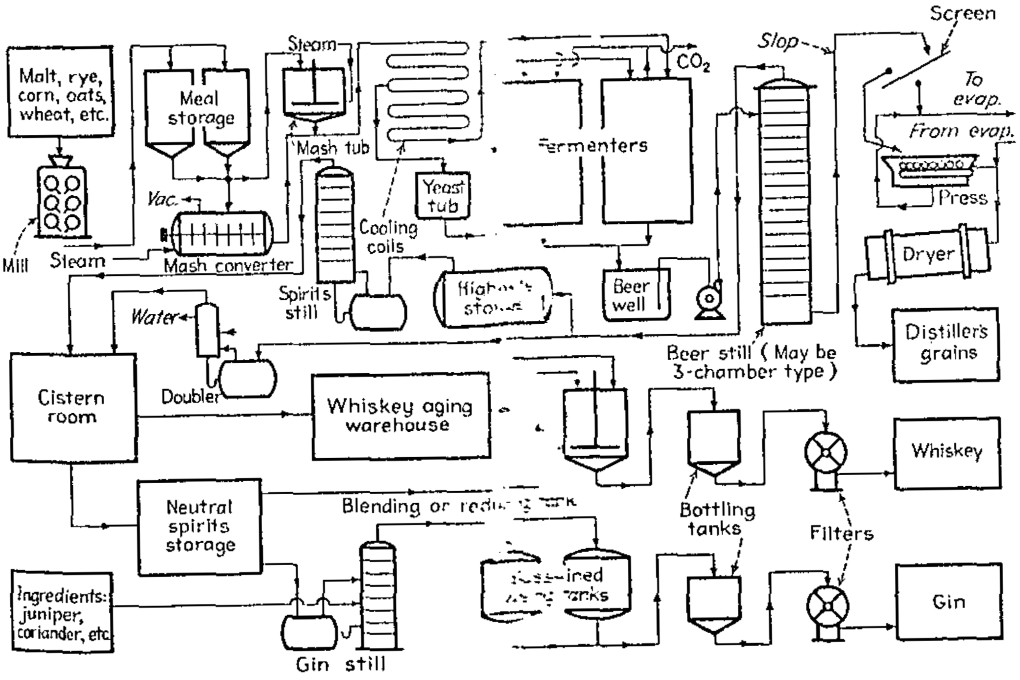

Fig. 31.6 Flowchart for distilled liquors.

TABLE 31.4 *U.S. Net Production of Distilled Spirits (In tax gallons, fiscal year)*

	1965	*1964*	*1963*	*1962*
Whisky	117,930,282	102,731,916	105,409,712	136,000,484
Brandy	11,521,724	11,142,801	8,602,539	7,548,382
Rum	2,273,811	2,128,832	2,078,356	1,743,779
Gin	25,560,827	23,625,545	21,858,754	20,667,009
Vodka	12,620,937	10,836,521	10,221,351	9,940,095
Alcohol and spirits:				
190° and over	658,640,527	647,818,852	618,164,806	604,254,667
Under 190°	36,691,486	40,693,628	34,494,453	29,363,219
Total	865,239,594	838,978,095	800,829,991	809,517,585

Source: Internal Revenue Statistics Release.

upon barreling to 100 to 110 proof. It is *not* pure alcohol but contains small amounts of many different constituents, generally classed together as *congenerics,* which by their reaction with each other or the alcohol, or by their absorption, all catalyzed by the char of the wood, help greatly in imparting the whisky flavor and bouquet.[1] The aging whisky also extracts color and other products from the charred white oak. Changes of a like nature occur similarly on aging brandy and rum. Here, as in other divisions of the fermentation industries, skill and scientific knowledge aid in the production of a palatable product. By law, whisky must be fermented from whole grains, so that the germs (containing the corn oil) and the husks are in suspension in the liquor from the beer still in whisky manufacture. This discharge liquor is known as *slop,* or *stillage.* As shown in Fig. 31.6, this is treated to recover the values by separating the solids from the liquid slop. After vacuum evaporation of the liquid[2] portion, it is added to the solids, and the mixture dried in rotating steam-heated dryers to produce *distillers' grains,*[3] a valuable cattle feed.

BUTYL ALCOHOL AND ACETONE

Until World War I, all the acetone produced in the United States was made by the dry distillation of calcium acetate from pyroligneous acid. Under the stimulus of the wartime demand for acetone for the manufacture of double-base smokeless powder, the important process became that developed by Chaim Weizmann[4] for the fermentation of starch-containing grains to butyl alcohol and acetone. The Commercial Solvents Corporation was organized, and it built and operated two plants in the Corn Belt to ferment corn, using *Clostridium acetobutylicum* bacteria. This fermentation, however, gave 2 parts of butyl alcohol to 1 part of acetone, and until the development of the fast-drying nitrocellulose lacquers, particularly for the automotive industry, there was virtually no market for the butyl alcohol produced. Then the conditions became reversed, with butyl alcohol

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[1] Liebmann and Scherl, Changes in Whisky Maturing, *I&EC,* **41**, 534 (1949).

[2] Cf. Boruff *et al.,* Vitamin Content of Distillers' By-products, *I&EC,* **32**, 123 (1940).

[3] For a pictured flowchart, see Recovery of Grain Alcohol By-products, *Chem. & Met. Eng.,* **52** (6), 130 (1945); Boruff, Industrial Wastes: Recovery of Fermentation Residues as Feeds, *I&EC,* **39**, 602 (1947).

[4] Brit. Pat. 4845 (1915); U.S. Pat. 1,315,585 (1919). Weizmann used much of his large royalties from this process to help finance his interest in the Zionist movement, of which he became the head in 1920.