VINEGAR

1. Introduction

Vinegar is the liquid condiment or food flavoring used to give a sharp or sour taste to foods. It is also used as a preservative in pickling and as the sour component in many different sauces, dressings, and gravies. Asian-style sweet–sour sauces and so-called health beverages are also based on vinegars . The word vinegar is derived from Latin via the old French *vinaigre*, meaning eager wine. In old English and old French the word eager (*aigre*) meant sour or sharp. Thus, vinegar is a sharp or sour wine and, as such, consists principally of water, acetic acid, mineral salts, and the organic constituents of the natural organic starting material.

Vinegar results from the action of the enzymes of bacteria of the genus *Acetobacter* and some others on dilute solutions of ethyl alcohol such as cider, wine, beer, or diluted distilled alcohol. Most vinegars for table use, eg, in the dressing of salads, derive from the acetic acid–bacterial fermentation of wine or cider. These latter, in turn, are produced by alcoholic fermentation (see FERMENTATION) of dilute sugar solutions such as grape juice, apple juice, or malt. *Saccharomyces cerevisiae* is the yeast involved most frequently in alcoholic fermentation, ie, in the enzymatic conversion of fermentable sugars to dilute alcoholic solutions (see YEASTS). Although fruits and honey are used most frequently as sources of fermentable sugar for vinegar production, barley malt and, in the Orient, rice, after hydrolysis of starch, serve as primary sources (see FOOD PROCESSING; FRUIT JUICE). Some raw materials used for vinegar production are listed in Table 1.

In the United States, standards of identity for vinegar date back to the Federal Food and Drug Act of 1906, in which six types of vinegar are defined as follows: "Vinegar, cider vinegar, apple vinegar, is the product made by the alcoholic and subsequent acetous fermentations of the juice of apples, and contains, in 100 cubic centimeters (20°C), not less than 4 grams of acetic acid" (33). The other five types of vinegar are defined in the same terms, except that cider vinegar is replaced by wine vinegar, malt vinegar, sugar vinegar, glucose vinegar, or spirit vinegar. In the case of the malt vinegar, the sugar of a hydrolyzed starch solution is fermented to ethanol. This solution, known as dilute beer, is immediately oxidized by *Acetobacter* to vinegar. The quantity of 4 g in 100 cm^3 of the quoted federal regulation (33) is equivalent to 40 g/L acetic acid, or 40-grain strength in the terms used by vinegar producers. The United States *Federal Register* carries regulatory announcements concerning vinegar production at frequent intervals.

A number of factors govern the composition of vinegar: the nature of the raw material, the substances added to promote alcoholic fermentation and the growth and activity of *Acetobacter*, the procedure used for the acetification, and finally the aging, stabilization, and bottling operations. Vinegars are made from natural solutions containing fermentable sugars, such as fruit juices and honey; solutions in which the sugars are produced by hydrolysis of starch, such as beers and sake; and solutions of distilled ethyl alcohol. Distilled alcohol, in turn, can be derived from the sugars of fruits or that from hydrolysis of starch,

or from synthetic processes such as the hydration of ethylene from petroleum. Most countries distinguish between fermentation vinegars and synthetic vinegars. Mediterranean countries usually permit only fermentation vinegars (some only wine vinegar) as foods, whereas in some northern European countries even dilute solutions of synthetic acetic acid are acceptable.

Grape and apple juices usually contain all of the trace nutrients required by *Saccharomyces* for fermentation of sugars to alcohol. Other fruit and diluted honey, as well as barley malt and rice extract, frequently need additions of nitrogen, phosphorus, and potassium compounds, together with some autolyzed yeast to facilitate the yeast growth necessary for fermentation. Stimulation of *Acetobacter* growth frequently requires the addition of autolyzed yeast, vitamin B complex and phosphates. The character and composition of vinegar is influenced greatly by the method used for the acetification and the subsequent processing steps.

2. Properties

2.1. pH. The pH of vinegar is typically in the range of 2–3.5 depending on the concentration of acetic acid.

2.2. Density. Vinegar has a density of approximately 0.96 g/mL.

2.3. Characteristics

White. Most white vinegars are 5% acetic acid solutions. They are made from grains, usually corn, and water.

Balsamic. Balsamic vinegar is an aromatic, aged type from the concentrated juices, or must, from white grapes. It is dark brown and its flavor is rich and complex. Balsamic vinegar is aged between 3–12 years or more in casks of various woods. Balsamic vinegar has a high acid level, but sweetness covers the tart flavor.

Rice. Rice vinegar is available in white, red, and black. It is popular in the cuisine of Eastern and South East Asia.

Cider. Cider vinegar is made from apples or cider and is sold unfiltered. It has a brownish yellow color.

Wine. Wine vinegar is made from red or white wine. It is the most commonly used vinegar in the Mediterranean countries and Central Europe. Better qualities are aged in wood for up to two years. They have a complex and mellow flavor.

Other Vinegars. Fruit vinegars are made from fruit wines, usually the favor of the original fruit remains. Malt vinegar is made from malting barley. The starch in the grain is turned to maltose. Ale is brewed from the maltose and then allowed to turn to vinegar.

Cane vinegar is made from sugar cane juice. Colors range from dark yellow to golden brown. It is popular in the Philippines.

Coconut vinegar is used in Southeast Asian cuisine. It is a cloudy white liquid and it has a sharp, acidic, yeasty taste.

Raisin vinegar is used in Middle Eastern Cuisine. It is cloudy, medium brown in color, and has a mild flavor.

3. Manufacture

Primitive people very likely encountered vinegar-like liquids in hollows in rocks or downed timber into which berries or fruit had fallen. Wild yeasts and bacteria would convert the natural sugars to alcohol and acetic acid. Later, when early peoples had learned to make wines and beers, they certainly would have found that these liquids, unprotected from air, would turn to vinegar. One can postulate that such early vinegars were frequently sweet, because the fruit sugars would have been acted on simultaneously by both bacteria and yeast. Only since the middle 1800s has it been known that yeast and bacteria are the cause of fermentation and vinegar formation.

3.1. Starch Hydrolysis and Alcoholic Fermentation. In general, because yeasts cannot utilize starch directly as a carbon source, the starch must first be hydrolyzed to sugar. Malt vinegars, commonly used as table vinegar in the United Kingdom, are made from malted barley or a mixture of malted barley with other starchy grains. Malt enzymes convert starch to sugars readily fermentable by *Saccharomyces* yeasts. In Japan, where vinegars are made from rice, a mixture of hydrolyzing enzymes produced by the fungus *Aspergillus oryzae* converts rice starches to sugars. A small amount of cooked rice cultured with the fungus is added to a larger quantity of cooled steamed rice. Frequently, the yeast that converts the sugar to alcohol is added at the same time, resulting in a dilute alcoholic solution rather than a dilute sugar solution. For the alcoholic fermentation itself, strains of *Saccharomyces cerevisiae* are most frequently used. The malt alcoholic solutions usually contain 5–10 vol % of ethanol; rice-derived alcoholic solutions, ie, sake, may contain 15–20%. These alcoholic solutions usually are converted immediately to vinegar but, if they are to be stored, the pH should be low enough to discourage growth of undesirable organisms. In particular, lactic bacteria can cause problems at higher pH values. Addition of 20–30 mg SO_2/L of vinegar helps to prevent undesirable bacterial activity during storage.

Alcoholic fermentation, according to the Gay-Lussac equation,

$$C_6H_{12}O_6 \rightarrow 2\,CO_2 + 2\,C_2H_5OH$$

yields 0.5114 g alcohol for each 1 g of sugar used. The theoretical yield is never obtained because of side reactions, volatilization of alcohol with the evolving carbon dioxide, competition from other organisms, and other factors (34). Yields of 88–94% are considered good commercial practice (see FERMENTATION).

The alcoholic fermentation is frequently conducted in two phases, although in a modern vinegar plant it can be conducted in one. The first phase is a vigorous fermentation during which the rapid evolution of carbon dioxide protects the alcoholic solution from air. The second or slower phase is fermentation of the residual sugar at a lower rate, during which, again, protection from air is required. In the first phase, 50–100 mg SO_2/L of sugar-containing mash is added, followed after approximately 1 h by 1–3% of an actively fermenting, pure-culture starter of *Saccharomyces cerevisiae*. The fermentation process is monitored for disappearance of sugar and increase in temperature. Rates of

alcoholic fermentation are highest at ca 25–30°C; higher temperatures tend to damage enzyme systems. The decrease in sugar content is measured hydrometrically and usually is expressed in degree Brix (the weight percentage of sucrose in a sucrose–water mixture). However, the sugar content of fruit juice of corresponding density is only slightly less than the equivalent percentage of glucose and fructose. Some error is introduced by the presence of nonsugar solids. Alcohol produced during the fermentation has a density less than that of water, causing the degree Brix reading to decrease more than it would from the loss of the sugar alone. Temperatures during the fermentation are controlled by cooling when necessary. Cooling jackets or internally mounted coils are used, although in older installations the fermenting medium is pumped from the tank through an external heat exchanger and returned to the tank. Near the end of the vigorous fermentation (about 0°Brix), the wine or beer is siphoned off and placed in another tank for final fermentation. Equipped to permit escape of CO_2 but prevent entry of air, this tank is used for fermentation of residual sugar. In a modern plant, the complete fermentation can be conducted in a single closed stainless steel tank. When all the sugar has been fermented (negative °Brix readings and <1 g/L reducing sugars), the wine or beer may be acetified immediately or stored protected from air. For prolonged storage, addition of 50 mg/L SO_2 helps to prevent growth of lactic organisms.

Both the fermentation of hexose sugars to ethanol and carbon dioxide and the oxidation of ethanol to acetic acid are exothermic (heat yielding) processes (see SUGAR). The first reaction is expressed as follows:

$$180\,\text{g}\,C_6H_{12}O_6 \rightarrow 92\,\text{g}\,C_2H_5OH + 88\,\text{g}\,CO_2 + 234\,\text{kJ}\,(55.6\,\text{kcal})$$

The yeast enzymes capture ca 92 kJ (22 kcal) of this energy for the formation of adenosine triphosphate (ATP), and the actual waste heat per 180 g (mol wt) of sugar fermented is ca 142 kJ (33.9 kcal). Depending upon the size of the fermenter and the rates of fermentation and aeration, loss of waste heat is apportioned among radiation, conduction, and vaporization of water and ethanol plus carbon dioxide. Although small fermenters may require no cooling, large ones require more cooling than occurs through natural radiation and conductance.

Wines have a low sodium and high potassium content and also contain tartaric, malic, and succinic acids, a wide spectrum of amino acids, phenolic materials, and trace quantities of vitamins and growth factors. These substances are found also in wine vinegar. Vinegar materials from other fruits, honey, and sugar-containing natural materials also contain a wide spectrum of nutrients from the base material. Distilled alcohol solutions, in contrast, do not contain nonvolatiles. Growth of acetobacter in these substrates requires addition of nitrogen, potassium, and phosphorus salts, trace amounts of other elements, and some organic growth factors.

3.2. Acetic Acid. Ethyl alcohol is converted to acetic acid by air oxidation catalyzed by the enzymes within bacteria of the genus *Acetobacter*:

$$46\,\text{g}\,C_2H_5OH + 32\,\text{g}\,O_2 \rightarrow 60\,\text{g}\,CH_3COOH + 18\,\text{g}\,H_2O + 487.2\,\text{kJ}\,(116.4\,\text{kcal})$$

One gram of ethanol should yield 1.304 g acetic acid. Practical yields are 77–85%. To avoid killing bacteria, excess heat must be removed during the course of the oxidation. For example, oxidation of 1 m^3 (264 gal) of a solution of ethanol (10% by volume) yields 836.7 MJ (ca 2×10^5 kcal). If this oxidation occurs over a 4-d period, and the heat is liberated at a uniform rate, heat production amounts of 2.42 kW.

In contrast with the well-known Embden-Meyerhof-Parnass glycolysis pathway for the conversion of hexose sugars to alcohol, the steps in conversion of ethanol to acetic acid remain in some doubt. Likely, ethanol is first oxidized to acetaldehyde and water (35). For further oxidation, two alternative routes are proposed: more likely, hydration of the acetaldehyde gives $CH_3CH(OH)_2$, which is oxidized to acetic acid. An alternative is the Cannizzaro-type disproportionation of two molecules of acetaldehyde to one molecule of ethanol and one molecule of acetic acid. Possibly *Acetobacter* initiates both reactions (36). The disproportionation reaction is favored by slightly alkaline pH values, whereas the dehydrogenation more readily occurs under acidic conditions. In slightly acid media such as wine and beer, dehydrogenation seems more likely than disproportionation.

3.3. Orleans Process. Early mention of vinegar is found in the Talmud, in accounts of wine and beer turning to vinegar (37). The Babylonians, ca 5000 BC, made and used vinegar as a flavor enhancer and as a pickling agent or preservative. Production of vinegar by the Greeks and Romans is described in numerous writings, but it was not until the fourteenth century that there are records of vinegar-making, in Modena, Italy, and near Orleans, France. In the Orleans process, the wine oxidizes slowly in a barrel where it is covered with a film of *Acetobacter*. Holes that are covered with screens to exclude insects are bored in each barrel head to permit access to air. Wine is added through the bung hole with a long-stemmed funnel below the surface of the bacterial film and without disturbing the film. In operation, vinegar is removed through a spigot mounted near the bottom of the barrel head and is replaced with an equivalent quantity of wine through the funnel. Wines with 10–12% ethanol give vinegars of 8–10% acetic acid concentration. Orleans vinegars are characterized by a relatively high concentration of ethyl acetate, detected by its pleasantly strong fruity odor. Although Orleans process wine vinegar is much preferred for table use, its production is slow and relatively costly and has been replaced for processing vinegars. Furthermore, the vinegar in the Orleans process barrels tends to become slimy from the production of exocellular bacterial cellulose generated by *Acetobacter xylinum*. This slimy cellulose, called mother of vinegar, encapsulates the bacterial cells and dramatically slows the rate of production. Significant amounts of red wine vinegar are produced in Europe by the Pasteur modification of the Orleans process. A wooden grating is placed at the surface of the liquid in the partially filled barrels or in shallow tanks to support the film of vinegar bacteria.

In 1973, a multistage surface-fermentation process was patented in Japan for the production of acetic acid (38); eight surface fermenters were connected in series and arranged in such a way that the mash passed slowly through the series without disturbing the film of *Acetobacter* on the surface of the medium. This

equipment is reported to produce vinegar of 5% acidity and 0.22% alcohol with a mean residency time in the tanks of 22 h.

3.4. Modena-Style or Balsamic Vinegar Process. Balsamic vinegars are made in and around the city of Modena in central Italy and consist of two general types: "Aceto Balsamico Tradizionale di Modena o di Reggio Emilia" and "Aceto Balsamico di Modena" (39). The traditional product is made from juice of the Trebbiano grape concentrated to about 40% sugar by direct flame heating of the container. The concentrate is added to the first (youngest) barrel of a series which is operated as a fractional blending system, the product removed from the oldest barrel being replaced by that from the one next older, and so forth through the system. The barrels are made of many different woods and vary considerably in size. *Zygosaccharomyces*, *Saccharomyces cerevisiae*, and *Gluconobacter* in the barrels convert the sugars to ethyl alcohol and gluconic acid as principal products. The ethyl alcohol is converted to acetic acid by the *Acetobacter* and *Gluconobacter*. Subsequent chemical and bacterial reactions result in the formation of many other flavor and odor substances, among the more important of which is the ester ethyl acetate. Years of age as the product passes through the blending system create a condiment exhibiting a harmonious balance of sweetness and tartness. Analysis of 99 aliquots from ten different Aceto Balsamico Traditionale systems of barrels showed increases of heavy metal cations (Cr, Ni, Cu, Zn, Cd, and Pb) with age (40). This indicates that evaporation of volatiles concentrated the nonvolatile metal salts in the product as it progressed through the system. Another analysis of product from each barrel of 13 systems showed increasing concentrations of gluconic acid with barrel age in about half of the systems and that gluconic acid concentration was significantly greater in Aceto Balsamico Traditionale than in Aceto Balsamico di Modena, wine and cider vinegars (39). Aceto Balsamico di Modena differs from the traditional product in that wine vinegar is blended into the grape juice concentrate and the age of the product is usually less.

3.5. Generator Process. References to quick or generator processes for vinegar production are found as early as the seventeenth century (41). Usually, generators are packed with shavings of beech wood, which tend to curl and thus provide packing that does not consolidate but allows open spaces for the free flow of liquid and air. In addition, beech wood does not contribute undesirable flavors or impurities to the vinegar. In the modern generator, a recirculating pump transfers the partially acetified alcoholic mixture from the bottom section of the generator to a distributing system at the top of the packed section. Air is measured into the upper part of the storage section below the packed section of the vat and exhaust air is vented from the top of the packed section to the outside, although in some generators it is recirculated (42). Cooling coils may be located in the packed section, but more frequently are placed at the bottom of the receiver section or are incorporated in the line for recirculating the liquid. Some packing materials other than the traditional beech wood shavings are coke, grape twigs, rattan bundles, corn cobs, or unglazed ceramic saddles. A pilot-plant Frings generator makes vinegar at a rate of 20.4 $\mu g L^{-1} s^{-1}$ (43).

Various species and many strains of *Acetobacter* are used in vinegar production (44,45). Aeration rates, optimum temperatures and nutrient requirements vary with individual strains. In general, fermentation alcohol substrates require

minimal nutrient supplementation while their addition is necessary for distilled alcohol substrates.

Submerged-Culture Generators. Adaptation of the surface-film growth procedure for producing antibiotics to an aerated submerged-culture process has been successful in making vinegar. A mechanical system keeps the bacteria in suspension in the liquid in the tank, in intimate contact with fine bubbles of air. The excess heat must be removed and the foam, which accumulates at the top of the tank, must be destroyed. The most widely used submerged-culture oxidizer is the Frings acetator (46). It uses a bottom-driven hollow rotor turning in a field of stationary vanes arranged in such a way that the air which is drawn in is intimately mixed with the liquid throughout the whole bottom area of the tank (47,48). In the United States, continuous cavitator units are used widely for cider-vinegar production.

A strain of thermophilic *Acetobacter* was patented in Japan for oxidizing ethanol in a submerged culture oxidizer at temperatures as high as 37°C with considerable savings in cooling water. Another thermophilic strain of *Acetobacter* maintained full activity at 35°C, and 45% of its maximum activity at 38°C.

A Frings acetator consisting of a 48-m^3 (12,700-gal) tank produces 12 m^3 (3,200 gal) of 10% acetic acid vinegar/d. It required 2.2 L of cooling water/s at 15°C and an energy input of ca 36MW (8600 kcal/s) (35). Thus, the submerged-culture oxidizer is capable of producing vinegar at nearly twice the rate of the best generator. Furthermore, submerged culture oxidizers are smaller for a given amount of production and, most important, they are more flexible in their operation. It is possible to change from one vinegar type to another with different feed-alcohol concentrations and nutrient requirements more quickly than with a generator.

Submerged-culture oxidizers are usually operated on a semicontinuous basis. In most cases, ca half the liquid in the tank is removed every 1–2 d, when the alcohol concentration has dropped to 0.1–0.2 vol %. The removed vinegar is replaced with wine or mash of richer ethanol and lower acetic acid concentration, giving a mixture in the tank of 5–6 vol % ethanol and 6–8 vol % of acetic acid. These are the optimum conditions for *Acetobacter* growth. Fermentation alcohol substrates do not require the addition of nutrients, but diluted distilled alcohol solutions need about 10–15 g of inorganic substances such as diammonium acid phosphate, potassium chloride, and traces of other metals and 30–50 g of organic materials such as glucose, autolyzed yeast, citric acid, and powdered whey per liter of alcohol. The pH of the fermenter mixture should be 3.9–5.0, the ideal temperature between 28 and 31°C. Since the new charge of mash or wine to the oxidizers lowers the temperature, cooling may be interrupted until the temperature again reaches 28–31°C. The rate of aeration depends on the surface of contact between air and liquid and is an inverse function of the bubble size. At optimum aeration rate, 50 mmol O_2/h is introduced into the solution per liter of mash, ie, 1870 cm^3 air/s/m^3 of mash. The maximum value for aeration recommended in Reference 35 is 1100 cm^3/s/m^3 mash.

Foam production is most troublesome under conditions adverse to bacterial growth and thus can be minimized by keeping nutrient, ethanol, and acetic acid concentrations in the optimum ranges. Temperature and aeration rate are also critical. Dead or dying cells seem to promote foam formation. Even under

optimum conditions, some type of foam breaker mounted in the top of the oxidizer is needed; the foam is usually broken down by centrifugal force, but food-grade silicone antifoaming agents may be employed.

Submerged culture oxidizers can also be operated on a continuous basis. Continuous monitoring of ethanol and acetic acid concentrations, temperature, and aeration rates permit control of feed and withdrawal streams. Optimum production, however, is achieved by semicontinuous operation because the composition of vinegar desired in the withdrawal stream is so low in ethanol that vigorous bacterial growth is impeded. Bacterial concentrations up to 100×10^6 cells/cm^3 have been reported in generators making about 20% vinegars.

A submerged-culture oxidizer with instrumentation to control the oxygen concentration of the mash accurately and with a heat-transfer system that efficiently controls the temperature is described in Reference (36). Clear vinegar may be withdrawn from the oxidizer by use of tangential filters which retain the bacteria in the system. Blinding of the filter is precluded by the rapid flow of liquid across the filter surface (49,50). The clear vinegar is removed from the system and the bacterial cells are retained to continue their work. Glycerol catalyzes the production of vinegar from the alcoholic solution obtained from malt wort (51), and its degradation pathways have been elucidated. Certain strains of *Saccharomyces cerevisiae* produce enough SO_2 to slow the start of oxidation by *Acetobacter* (52). A scrubber has been patented which greatly increases the efficiency of vinegar production by recycling ethanol and acetic acid vapors normally lost with the exhaust air stream (53).

3.6. Fluidized-Bed Vinegar Reactors. Intimate contact of air with *Acetobacter* cells is achieved in fluidized-bed or tower-type systems. Air introduced through perforations in the bottom of each unit suspends the mixture of liquid and microorganisms within the unit. Air bubbles penetrating the bottom plate keep *Acetobacter* in suspension and active for the ethanol oxidation in the liquid phase. Addition of a carrier for the bacterial cells to the liquid suspension is reported to improve the performance (54–56).

3.7. Vinegars with High Concentrations of Acetic Acid. The U.S. regulations require at least 4 g acetic acid/100 cm^3 vinegar. Commercial vinegar and many quality table vinegars are significantly more concentrated. Submerged-culture oxidizers easily give acetic acid concentrations of 10–13 g/cm^3. Production rate is somewhat less than for lower acetic acid concentrations. Submerged-culture oxidizer techniques that produce vinegars with acetic acid concentrations ranging from 15–20% are now in commercial use (57–59). Continuous aeration, careful stepwise addition of ethanol as it is oxidized and careful control of temperature seem to be the keys to successful operation. The increased oxidation rate is the result of a greater cell mass per unit volume and of the selection of bacteria more tolerant of ethanol and of acetic acid (60–62).

In order to obtain ever higher acetic acid concentrations, water is removed after the generation step by freezing (63–66). Ice crystals are removed from the slush by filtration or centrifugation. Concentrated vinegars are of particular value in the pickling industry where dilution of the vinegary, spiced mixture by the water from the cucumbers is a serious and costly problem (36). Concentrated wine vinegar is stabilized with bentonite, silica gel, or $K_4Fe(CN)_6$. In

another process, water is removed by formation of a hydrate of trichlorofluoromethane. The solid hydrate is separated from the concentrated vinegar and the fluorocarbon is recovered and recycled (67) (see INCLUSION COMPOUNDS). In another suggested process, vinegar acetic acid is neutralized with Na_2CO_3 and the water is removed by reduced-pressure distillation. H_2SO_4 is then added to liberate the acetic acid, which is removed by low pressure distillation (68). Production of a very high acetic acid (40%) vinegar by extraction of normal (15%) vinegar with liquid CO_2 under pressure is described in a Japanese patent application (69).

3.8. Vinegar Eels and Mother of Vinegar. The nematode *Anguilla aceti* grows readily in packed-tank vinegar generators. Although it is esthetically undesirable, it is not harmful. These nematodes, known as vinegar eels, may actually be of some assistance in consuming dead bacteria from the surface of the packing material in the tank, and thus may aid in prolonging the operation of the system. Vinegar eels may also make nutrients more readily available to *Acetobacter* (70). Vinegar eels are removed from the raw vinegar by filtration and pasteurization before the vinegar is sold or used further in pickling or other processes.

Mother of vinegar is the term given to the cellulosic slime that coats the bacterial cells and is produced by a strain of *Acetobacter xylinium*. Different strains and different medium compositions result in different consistencies and crystalline forms of the cellulosic slime. Although it does not cause any problems in submerged-culture oxidizers, the slime can effectively block the passageways in packed-tank generators. High concentrations of acetic acid in the vinegar and the generator discourage the production of mother of vinegar slime.

4. Processing and Preparation for Marketing

4.1. Clarification. Raw vinegars as removed from the production unit vary widely in stability, depending upon the raw material and the type of generator or oxidizer employed. Table vinegars produced from wine, cider, malt, or other natural materials frequently contain unstable phenolic materials, pectins, and traces of proteins which form clouds or deposits. Vinegars from distilled alcohol are more stable, but still might contain traces of unstable materials. Generator vinegars are relatively free of *Acetobacter* cells, in contrast to the submerged-culture vinegars, which carry a high and cloudy suspension of bacterial cells. Clarification and stabilization of vinegars generally follow the standard practices of beverage industries. Bentonite is used as clarifier and, occasionally a proprietary formulation of potassium ferrocyanide is used to remove traces of heavy metals. Submerged-culture vinegar is clarified with mixed suspensions of bentonite and alginic acid (71); treatment with bentonite prepared with $NaHCO_3$ has been patented (72). Japanese patents describe vinegar stabilization with alumina or silica gels (73,74) or poly(vinylpyrrolidinone), cellulose, and Dowex A-1 for the same purpose. A Polish patent application describes vinegar clarification by foaming. Aeration is interrupted momentarily and then resumed vigorously for 5 min, creating a layer of foam amounting to $\sim$1% of the tank volume. The clearer liquid from the bottom portion of the tank is reported to

remain clear and stable (75). Activated carbon adsorbs some compounds causing clouding or precipitates in bottled vinegars. Vinegars are usually given a rough filtration on plate-and-frame or leaf filters with pads coated with diatomaceous earth. Immediately before bottling, the vinegar is filtered through more retentive pads or possibly membranes of pore size small enough to exclude all yeasts cells and bacteria. Membrane filtration can be combined with aseptic bottling to provide a vinegar free of all microorganisms, but the process is expensive and not essential to the stability of bottled vinegars. A membrane can be used for continuous microfiltration of cloudy vinegar (76,77). The surface is kept clean with a vigorous flow of liquid across the membrane parallel to its surface. This method has been successful in both laboratory and pilot plant.

4.2. Sterilizing and Packing. Many vinegars bottled for table use or pickling are pasteurized before shipment. In the low strength vinegars, the cellulose-producing acetic bacteria and certain strains of lactic bacteria may create problems. The former cause clouding, whereas the latter alter the flavor. Small amounts of sulfur dioxide are frequently added to minimize lactic-organisms' growth. Sterile filtration through very tight pads or through membranes followed by aseptic bottling is possible but difficult in the case of bacterial contaminants. For pasteurization, vinegar may be heated in bulk to 65–70°C, filled hot into bottles, sealed, and cooled slowly, or filled and sealed bottles may be pasteurized by heating to 65–70°C. Sterilization of many submerged-culture vinegars with high bacterial cell concentrations requires a pasteurization temperature of 77–80°C. The vinegar must be protected from exposure to bacterial or yeast contaminants and iron or copper in all processing steps following stabilization, ie, the filling equipment must be of stainless steel, plastic, or glass (see STERILIZATION TECHNIQUES).

5. Economic Aspects

Vinegar sales growth at 15% was stronger from 2000–2002 than most comparative categories. According to supermarket sales data, vinegar sales increased 29% from 1993 to 2003 (see Fig. 1) (78).

Shares of vinegar types for 2005 are listed in Table 2 (79).

Overall nonfood global introductions containing vinegar increased 131% between 2004–2005. Household products accounted for 50% of these uses. Nonfood introductions increased significanty in Asia Pacific and Europe and accounted for 86% of activity in 2005.

6. Standards for Labeling

The following varieties of vinegar are classified by a U.S. Food and Drug Administration (FDA) Compliance Policy Guide for labeling purposes according to their starting material and method of manufacturing (80)

Cider vinegar of apple vinegar is made from the two-fold fermentation of the juices of apples. Vinegar can be made from other fruits such as peaches and berries with the labels describing starting materials.

Wine vinegar or Grape vinegar is made from the two-fold fermentation of the juice of grapes.

Malt vinegar, made by the two-fold fermentation of bareley malt or other cereals where starch has been converted to maltose.

Sugar vinegar, made by the two-fold fermentation of solutiosn of sugar syrup or molasses.

Spirit or distilled vinegar, made by the acetic fermentation of dilute distilled alcohol.

Blended vinegar made from a mixture of spirit vinegar and cider vinegar is considered a combination of the products that should be labeled with the product names in the order of predominance. It is also the product made by the two-fold fermentation of a mixture of alcohol and cider stock.

Rice or rice wine vinegar (although not part of FDA's Compliance Policy Guide) has increased in popularity over the past several years and is made by the two-fold fermentation of sugars from rice or a concentrate of rice without distillation. Seasoned rice or rice wine vinegars are made from rice with the "seasoning" ingredients noted on the label.

Balsamic vinegar (also not a part of FDA's Compliance Policy Guide) continues to grow in market share and "traditional" and "commercial" forms are available. The products are made from the juice of grapes, and some juice is subjected to an alcoholic and subsequent acetic fermentation and some to concentration or heating.

7. Analyses of Vinegars

Because there is a considerable difference in cost between vinegar derived from petroleum-based or other synthetic ethanols and that derived from present-day biogenic sources such as grapes, apples, barley, or rice, there has always been need for analytical methods to detect blending. The presence of ^{14}C and ^{3}H in the methyl group of vinegar acetic acid is evidence of recent biogenic origin. Vinegar from petroleum alcohol has none of these unstable carbon and hydrogen isotopes (81,82). Some success has been attained in differentiating among biogenic vinegars on the basis of $^{13}C/^{12}C$ and $^{2}H/3^{1}H$ isotopic ratios in the methyl group of the acetic acid of the vinegar (83–90) and by statistical studies of concentrations of minor compounds which differ with different sugar sources (91,92).

8. Uses

8.1. Culinary. Vinegar is used in food preparation, particularly in pickling, vinaigrettes, and other salad dressings. It is used as an ingredient in sauces such as ketchup, mustard, and mayonnaises. It is a component of

chutney. Marinades often contain vinegar. Vinegar is used as a condiment and as a substitute for lemon.

8.2. Cleaning Aides. White vinegar is used as a natural household cleaning agent. It is especially useful in cleaning mineral deposits from smooth surfaces. Commercial vinegar for household use does not exceed 5%. Careful handing is needed since the solutions are corrosive and damaging to skin and eyes. It is also used in hair and skin care products.

8.3. Medicinal. Many remedies and treatments have been ascribed to vinegar throughout history. Not many have been verified by medical trials. Some recent documented uses include control of blood glucose (93,94) and diet control (95,96). In veterinary treatments, it is used as a bactericide and digestive aid. Recent U.S. patents cite the use of vinegar and baking soda in foaming oral care preparations (97), and the use of vinegar acid to treat dermomycosis (98).

8.4. Agricultural. Vinegar can be used as a herbicide. Vinegar is made from natural products and is classified as organic so there is interest in the use of vinegar on farms and in orchards and gardens. Common weeds can be effectively controlled using vinegar with 5–20% acetic acid (99).

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Table 1. **Raw Materials Used to Make Vinegar**

Raw material	Reference	Raw material	Reference
Mainly sugary		*Mainly starchy*	
jujube	4	potato, corn flour	22
sweet potato	5	soybean	23
dates	(6,7)	seaweed	24
citrus	(8,9)	rice	25
persimmon	(10,11)	grain starch	26
pear	12		
sugar cane	13	*Various*	
plum	14	onions	27
tomato	15	bamboo grass	28
kiwi fruit	16	wood	29
pineapple	17	whey	30
molasses	18	coconut water	31
honey	19	vinasse (distillation residue)	32
palm sap	20		
muscavado (brown sugar)	21		

Table 2. **Shares of Vinegar Types, %**

Type	North America	Global
white	1	2
balsamic	45	34
rice	8	4
cider	8	7
red wine	13	17
other	25	36

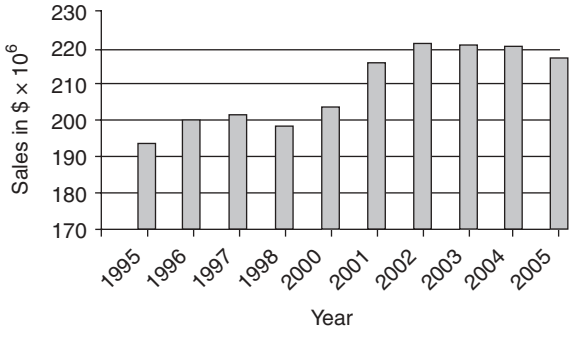

Fig. 1. Supermarket sales of bottled vinegar.