VINEGAR AND ACETIC ACID

The aerobic bacterial oxidation (by the genus *Acetobacter*) of alcohol to dilute acetic acid (8%) is another ancient procedure, furnishing vinegar, a flavored acetic acid solution, fermented from wine, cider, malt, or dilute alcohol. If pure dilute alcohol is fermented, pure dilute acetic acid results. The yield is 80 to 90% of theory. Air[32] must be supplied, as these formulations indicate:

$$2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O \quad 2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

Since these reactions are exothermic, either the alcohol can be slowly trickled through the apparatus, letting the heat dissipate, or it can be recirculated with special cooling. If cider, malt, or wine is fermented, the acetic acid content of the resulting vinegar rarely exceeds 5% because of limitations of the sugar content; if dilute alcohol is the raw material, the acetic acid may rise to 12 or 14% at which acidity the bacteria cease to thrive. If a fruit juice is turned to vinegar, certain esters are formed, varying with the raw material and thus imparting a characteristic flavor. Synthetic acetic acid is made from ethylene, or by treating methanol with carbon monoxide.

CITRIC ACID

Citric acid is one of our most versatile organic acids. Its major use is as an acidulant in carbonated beverages, jams, jellies, and other foodstuffs. Another large outlet is in the medicinal field, including the manufacture of citrates and effervescent salts. Industrial uses, relatively small, include citric acid as an ion-sequestering agent buffer and acetyl tributyl citrate, a vinyl resin plasticizer. Citric acid is meeting competition from other organic acids, for example, fumaric, maleic, and adipic.

Except for small amounts (less than 7 percent) produced from citrus-fruit wastes, citric acid is manufactured[33] by aerobic fermentation of crude sugar or corn sugar by a special strain of *Aspergillus niger*, following the classical research by Currie. The overall reactions are

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + 3O_2 \rightarrow 2C_6H_8O_7 + 4H_2O$$

$$\underset{\text{Dextrose}}{C_6H_{12}O_6} + 1\tfrac{1}{2}\,O_2 \rightarrow \underset{\text{Citric acid}}{C_6H_8O_7} + 2H_2O$$

The fermentation changes sugar and dextrose, straight-chain compounds, into branched chains. An earlier shallow-tray fermentation process was abandoned because of the expensive manual processing and the development of the submerged process.

The submerged process for the manufacture of citric acid is depicted in Fig. 4.7, and this

---

[32]Too much air causes losses because of further and undesired oxidation; ECT, 3d ed., vol. 6, 1979, pp. 150–173.

[33]Currie, The Citric Acid Fermentation of *A. niger*, *J. Biol. Chem.* 31 15 (1917).

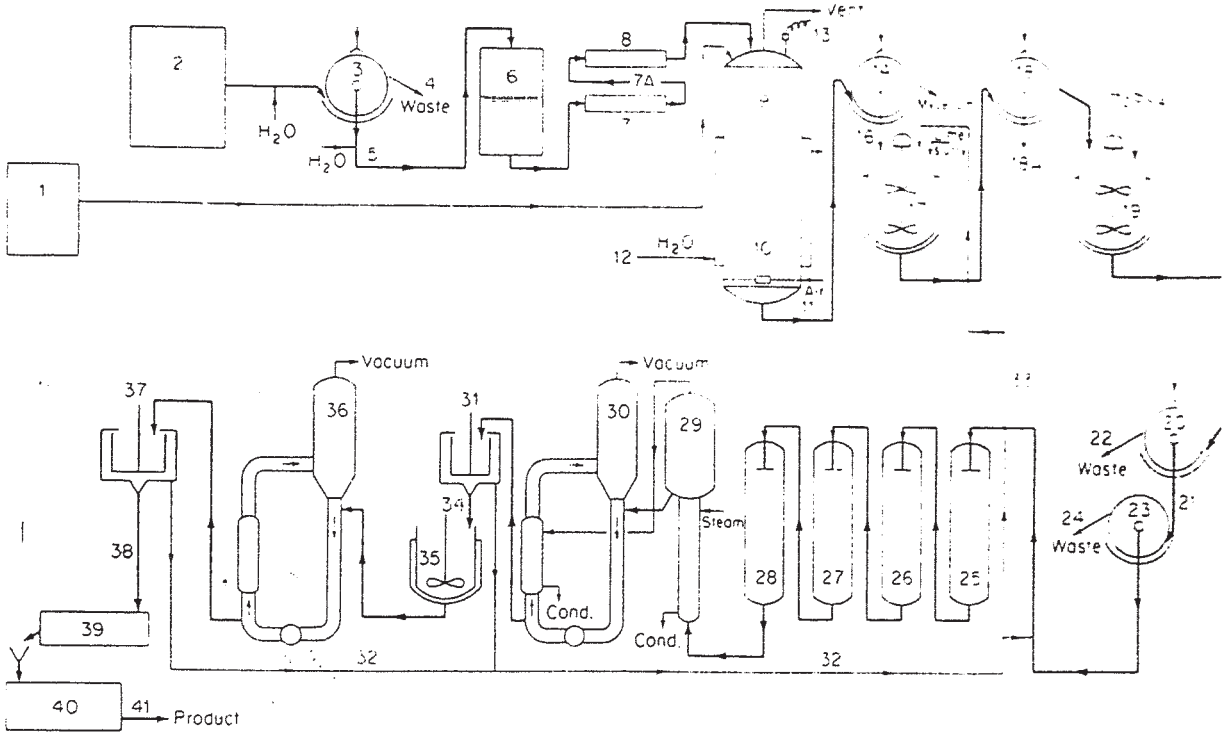

Fig. 4.7. Flowchart for citric acid production. The purification of the dextrose glucose syrup is fundamental (nos. 2 through 8), involving a rotary vacuum filter (3) to remove suspended or precipitated solids after partial dilution. This is followed by a cation-exchange cell (6) for trace-element reduction and a flash pasteurization heater (7), holding loop (7a), and syrup cooler (8). The syrup is pumped into the fermentor (9) plus inoculum (1). The pH adjustment is made and nutrients added. Sterile air (11) from filters and flowmeters is sparged (10) into the fermentor (9). The fermentation process for the production of citric acid is, in its simplest terms, the conversion of a molecule of a hexose sugar to a six-carbon molecule of citric acid (9). The purification and recovery of the resultant acid are then basically an application of the lime-sulfuric scheme first used by Scheele in 1784. Today's methods involve first separating off the mycelium (14) from the broth, which contains the citric acid (16), liming it with milk-of-lime slurry (17), filtering off and washing the resultant calcium citrate (18), and finally decomposing the citrate with sulfuric acid (19). The calcium sulfate formed from this decomposition is filtered off as a waste by-product (20, 23). The more modern plants of today perform these three filtrations on some form of rotary vacuum filter. The further purification of the decomposed liquor from the sulfuric decomposition is variable from manufacturer to manufacturer. This figure indicates treatment with granular carbon in fixed beds (25, 26), followed by demineralizing beds containing cation- and anion-exchange resins (27, 28). Double-or triple-effect evaporators (29) feed a separate crystallizer (30) and centrifuge (31). The mother liquor is recycled between feed to carbon cells (32) or to a liming tank (33). The damp citric acid crystals are remelted (35) and vacuum crystallized (36). This is followed by centrifuging (37), drying (39), size classification (40), and packaging (41). The degree of purity of the initial sugar source going into the fermentation can be a factor in determining the amount of purification necessary and the need for recrystallizing the final product. *(Miles Laboratories, Inc.)*

may be broken down into coordinated sequences of biochemical conversions with the aid of *A. niger* and various unit operations and chemical conversions. A selected strain of *A. niger* is grown from a test-tube slant through to a seed tank, or inoculum. This growth may take 36 to 48 h. For sequential steps see the description below Fig. 4.7.

Special strains of yeast, *Candida guillier mondii* and *Candida lipolytica*, have been developed to produce citric acid. *C. lipolytica*[34] produces it from paraffin in a continuous process.

[34]U.S. Patent 4,014,742.

LACTIC ACID

Lactic acid, 2-hydroxypropionic acid, is one of the oldest known organic acids. It is the primary acid constituent of sour milk, where it derives its name, being formed by the fermentation of milk sugar (lactose) by *Streptococcus lactis*. Commercially, lactic acid is manufactured by controlled fermentation of the hexose sugars from molasses, corn, or milk. Lactates are made by synthetic methods from acetaldehyde and lactonitrile, a by-product of Monsanto's[35] acrylonitrile operation. It has been only since 1930 that lactic acid has been produced commercially from the milk by-product whey. About 1×10^9 kg of dry whey is produced annually from cheese or casein production, and about half is wasted.[36] The technical grade is employed for deliming leather in tanning. Edible grades are used primarily as acidulants for a number of foods and beverages. The small amount of lactic acid remaining is converted into plastics, solvents, and certain other chemical products. The USP grade is an old, well-established standard pharmaceutical.

MISCELLANEOUS COMPOUNDS

MONOSODIUM GLUTAMATE. The amino acid glutamic acid may be prepared synthetically, but chemical preparation produces a racemic mixture. Since only the sodium salt of the naturally occurring L-glutamic acid is desired for food flavor enhancement, this necessitates an expensive resolution step. L-Glutamic acid can be obtained directly from fermentation of carbohydrates with *Micrococcus glutamicus* or *Brevibacterium divaricatum*. Many patents have been issued on variations of the process as this is one of the largest volume compounds produced by fermentation.[37]

L-LYSINE. L-Lysine may be formed by microorganisms acting on carbohydrates. The usual organisms are *Micrococcus glutamicus*, *Brevibacterium flavum*, *Corynebacterium acetoglutamicum*, and *Microbacterium ammoniaphilum*. Each of these organisms requires special conditions and/or special additives to produce the product in good yields.

DIHYDROXYACETONE. Dihydroxyacetone ($HOCH_2COCH_2OH$) is made by the action of sorbose bacterium fermentation of glycerin.[38] This is an ingredient of suntan lotion that creates an artificial tan. It is also valuable as a chemical intermediate and as a catalyst in butadiene-styrene polymerization. Fatty acid esters of the hydroxyl groups are excellent emulsifying agents.

PHARMACEUTICAL PRODUCTS. The pharmaceutical industry has long employed fermentation (biosynthesis) to manufacture some of its most important medicaments. See Chap. 40, where fermentation is presented for antibiotics, biologicals, vitamins, and hormones. Controlled microorganisms are a most important chemical processing agent and assist in performing very complicated chemical reactions, in many cases more economically than purely

---

[35]Synthetic Lactic Acid, *Ind. Eng. Chem.* 51 (2) 55 (1964); *Chem. Eng.* 71 (2) 82 (1964).

[36]Fermentation Process Turns Whey into Valuable Protein, *Chem. Eng.* 82 (6) 36 (1975).

[37]Gutcho, *Chemicals by Fermentation*, Noyes, Park Ridge, N.J., 1973.

[38]U.S. Patent 2,948,658