ACETIC ACID

1. Introduction

Acetic acid [64-19-7], CH_3COOH, is a corrosive organic acid having a sharp odor, burning taste, and pernicious blistering properties. It is found in ocean water, oilfield brines, rain, and at trace concentrations in many plant and animal liquids. It is central to all biological energy pathways. Fermentation of fruit and vegetable juices yields 2–12% acetic acid solutions, usually called vinegar (qv). Any sugar-containing sap or juice can be transformed by bacterial or fungal processes to dilute acetic acid.

Theophrastos (272–287 BC) studied the utilization of acetic acid to make white lead and verdigris [52503-64-7]. Acetic acid was also well known to alchemists of the Renaissance. Andreas Libavius (AD 1540–1600) distinguished the properties of vinegar from those of icelike (glacial) acetic acid obtained by dry distillation of copper acetate or similar heavy metal acetates. Numerous attempts to prepare glacial acetic acid by distillation of vinegar proved to be in vain, however.

Lavoisier believed he could distinguish acetic acid from acetous acid, the hypothetical acid of vinegar, which he thought was converted into acetic acid by oxidation. Following Lavoisier's demise, Adet proved the essential identity of acetic acid and acetous acid, the latter being the monohydrate, and in 1847, Kolbe finally prepared acetic acid from the elements.

Worldwide demand for acetic acid in 1999 was 2.8×10^6 t (6.17×10^9 lb). Estimated demand for 2003 is 3.1×10^6 t (6.84×10^9 lb) (1). Uses include the manufacture of vinyl acetate [108-05-4] and acetic anhydride [108-24-7]. Vinyl acetate is used to make latex emulsion resins for paints, adhesives, paper coatings, and textile finishing agents. Acetic anhydride is used in making cellulose acetate fibers, cigarette filter tow, and cellulosic plastics.

2. Physical Properties

Acetic acid, fp 16.635°C (2), bp 117.87°C at 101.3 kPa (3), is a clear, colorless liquid. Water is the chief impurity in acetic acid although other materials such as acetaldehyde, acetic anhydride, formic acid, biacetyl, methyl acetate, ethyl acetoacetate, iron, and mercury are also sometimes found. Water significantly lowers the freezing point of glacial acetic acid as do acetic anhydride and methyl acetate (4). The presence of acetaldehyde [75-07-0] or formic acid [64-18-6] is commonly revealed by permanganate tests; biacetyl [431-03-8] and iron are indicated by color. Ethyl acetoacetate [141-97-9]may cause slight color in acetic acid and is often mistaken for formic acid because it reduces mercuric chloride to calomel. Traces of mercury provoke catastrophic corrosion of aluminum metal, often employed in shipping the acid.

The vapor density of acetic acid suggests a molecular weight much higher than the formula weight, 60.06. Indeed, the acid normally exists as a dimer (5), both in the vapor phase (6) and in solution (6). This vapor density anomaly has important consequences in engineering computations, particularly in distillations.

Table 1. **Acetic Acid–Water Freezing Points**

Acetic acid, wt %	Freezing point, °C
100	16.635
99.95	16.50
99.70	16.06
99.60	15.84
99.2	15.12
98.8	14.49
98.4	13.86
98.0	13.25
97.6	12.66
97.2	12.09
96.8	11.48
96.4	10.83
96.0	10.17

Acetic acid containing <1% water is called glacial. It is hygroscopic and the freezing point is a convenient way to determine purity (8). Water is nearly always present in far greater quantities than any other impurity. Table 1 shows the freezing points for acetic acid–water mixtures.

The Antoine equation for acetic acid has recently been revised (3)

$$\ln(P) = 15.19234 + (-3654.622)/T + (-45.392)$$

The pressure P is measured in kelopascal (kPa) and the temperature T in kelvin (K). The vapor pressure of pure acetic acid is tabulated in Table 2. Precise liquid density measurements are significant for determining the mass of tank car quantities of acid. Liquid density data (9) as a function of temperature are given in Table 3.

Acetic acid forms a monohydrate containing ~23% water; thus the density of acetic acid–water mixtures goes through a maximum between 77 and 80 wt %

Table 2. **Acetic Acid Vapor Pressure**

Temperature, °C	Pressure, kPa[a]	Temperature, °C	Pressure, kPa[a]
0	4.7	110	776.7
10	8.5	118.2	1013
20	15.7	130	1386.5
30	26.5	140	1841.1
40	45.3	150	2461.1
50	74.9	160	3160
60	117.7	170	4041
70	182.8	180	5091
80	269.4	190	6333
90	390.4	200	7813
100	555.3	210	9612

[a] To convert kPa to psi, multiply by 0.145.

Table 3. **Density of Acetic Acid (Liquid)**

Temperature, °C	Density, kg/m^3
20	1049.55
25	1043.92
30	1038.25
47	1019.19
67	996.46
87	973.42
107	949.90
127	925.60
147	900.27
167	873.56
187	845.04
197	829.88
207	814.07
217	797.44

acid at 15°C. When water is mixed with acetic acid at 15–18°C, heat is given off. At greater acetic acid concentrations, heat is taken up. The measured heat of mixing is consistent with dimer formation in the pure acid. The monohydrate, sometimes called acetous acid, was formerly the main article of commerce. Data on solidification points of aqueous acetic acid mixtures have been tabulated, and the eutectic formation mapped (10). The aqueous eutectic temperature is about −26°C. A procedure for concentrating acetic acid by freezing, hampered by eutectic formation, has been sought for some time. The eutectic can be decomposed through adding a substance to form a compound with acetic acid, eg, urea or potassium acetate. Glacial acetic acid can then be distilled. The densities of acetic acid–water mixtures at 15°C are given in Table 4.

A summary of the physical properties of glacial acetic acid is given in Table 5.

Table 4. **Density of Aqueous Acetic Acid**

Acetic acid, wt %	Density, g/cm^3
1	1.007
5	1.0067
10	1.0142
15	1.0214
20	1.0284
30	1.0412
40	1.0523
50	1.0615
60	1.0685
70	1.0733
80	1.0748
90	1.0713
95	1.0660
100	1.0550

Table 5. **Properties of Glacial Acetic Acid**

Property	Value	Reference
freezing point, °C	16.635	2
boiling point, °C	117.87	5
density, g/mL at 20°C	1.0495	9
refractive index, $n^{25}{}_{\mathrm{D}}$	1.36965	11
heat of vaporization ΔH_v, J/g[a] at bp	394.5	12
specific heat (vapor), J/(g·K)[a] at 124°C	5.029	12
critical temperature, K	592.71	3
critical pressure, MPa[b]	4.53	3
enthalpy of formation, kJ/mol[a] at 25°C		
liquid	−484.50	13
gas	−432.25	13
normal entropy, J/(mol·K)[a] at 25°C		
liquid	159.8	14
gas	282.5	14
liquid viscosity, mPa (=cP)		
20°C	11.83	15
40°C	8.18	15
surface tension, mN/m (=dyn/cm) at 20.1°C	27.57	16
flammability limits, vol % in air	4.0 to 16.0	16
autoignition temperature, °C	465	
flash point, °C		17
closed cup	43	
open cup	57	

[a] To convert J to cal, divide by 4.184.

[b] To convert MPa to psi, multiply by 145.

3. Chemical Properties

3.1. Decomposition Reactions. Minute traces of acetic anhydride are formed when very dry acetic acid is distilled. Without a catalyst, equilibrium is reached after ~7 h of boiling, but a trace of acid catalyst produces equilibrium in 20 min. At equilibrium, ~4.2 mmol of anhydride is present per liter of acetic acid, even at temperatures as low as 80°C (18). Thermolysis of acetic acid occurs at 442°C and 101.3 kPa (1 atm), leading by parallel pathways to methane [72-82-8] and carbon dioxide [124-38-9], and to ketene [463-51-4] and water (19). Both reactions have great industrial significance.

Single pulse, shock tube decomposition of acetic acid in argon involves the same pair of homogeneous, molecular first-order reactions as thermolysis (20). Platinum on graphite catalyzes the decomposition at 500−800 K at low pressures (21). Ketene, methane, carbon oxides, and a variety of minor products are obtained. Photochemical decomposition yields methane and carbon dioxide and a number of free radicals, which have complicated pathways (22). Electron impact and gamma rays appear to generate these same products (23). Electron cyclotron resonance plasma made from acetic acid deposits a diamond [7782-40-3] film on suitable surfaces (24). The film, having a polycrystalline structure, is a useful electrical insulator (25) and widespread industrial exploitation of diamond films appears to be on the horizon (26).

3.2. Acid–Base Chemistry. Acetic acid dissociates in water, $pK_a = 4.76$ at 25°C. It is a mild acid that can be used for analysis of bases too weak to detect in water (27). It readily neutralizes the ordinary hydroxides of the alkali metals and the alkaline earths to form the corresponding acetates. When the crude material pyroligneous acid is neutralized with limestone or magnesia the commercial acetate of lime or acetate of magnesia is obtained (8). Acetic acid accepts protons only from the strongest acids, such as nitric acid and sulfuric acid. Other acids exhibit very powerful, superacid properties in acetic acid solutions and are thus useful catalysts for esterifications of olefins and alcohols (28). Nitrations conducted in acetic acid solvent are effected because of the formation of the nitronium ion, NO_2^+. Hexamethylenetetramine [100-97-0] may be nitrated in acetic acid solvent to yield the explosive cyclotrimethylenetrinitramine [121-82-4], also known as cyclonit or RDX.

3.3. Acetylation Reactions. Alcohols may be acetylated without catalysts by using a large excess of acetic acid.

$$CH_3COOH + ROH \longrightarrow CH_3COOR + H_2O$$

The reaction rate is increased by using an entraining agent such as hexane, benzene, toluene, or cyclohexane, depending on the reactant alcohol, to remove the water formed. The concentration of water in the reaction medium can be measured, either by means of the Karl-Fischer reagent, or automatically by specific conductance and used as a control of the rate. The specific electrical conductance of acetic acid containing small amounts of water is given in Table 6.

Nearly all commercial acetylations are realized using acid catalysts. Catalytic acetylation of alcohols can be carried out using mineral acids, eg, perchloric acid [7601-90-3], phosphoric acid [7664-38-2], sulfuric acid [7664-93-9], benzenesulfonic acid [98-11-3], or methanesulfonic acid [75-75-2], as the catalyst. Certain acid-reacting ion-exchange resins may also be used, but these tend to decompose in hot acetic acid. Mordenite [12445-20-4], a decationized Y-zeolite, is a useful acetylation catalyst (29) and aluminum chloride [7446-70-0], Al_2Cl_6, catalyzes *n*-butanol [71-36-3] acetylation (30).

Table 6. **Specific Conductance of Aqueous Acetic Acid**

Acetic acid, wt %	Specific conductance κ, S/cm × 10^7
100	0.060
99.9515	0.065
99.746	0.103
99.320	0.261
98.84	0.531
97.66	2.19
96.68	5.45
94.82	20.1
92.50	59.9
90.75	111
82.30	688

Olefins add anhydrous acetic acid to give esters, usually of secondary or tertiary alcohols: propylene [115-07-1] yields isopropyl acetate [108-21-4]; isobutylene [115-11-7] gives *tert*-butyl acetate [540-88-5]. Minute amounts of water inhibit the reaction. Unsaturated esters can be prepared by a combined oxidative esterification over a platinum group metal catalyst. For example, ethylene-air-acetic acid passed over a palladium–lithium acetate catalyst yields vinyl acetate.

Acetylation of acetaldehyde to ethylidene diacetate [542-10-9], a precursor of vinyl acetate, has long been known (8), but the condensation of formaldehyde [50-00-0] and acetic acid vapors to furnish acrylic acid [97-10-7] is more recent (31). These reactions consume relatively more energy than other routes for manufacturing vinyl acetate or acrylic acid, and thus are not likely to be further developed. Vapor-phase methanol–methyl acetate oxidation using simultaneous condensation to yield methyl acrylate is still being developed (29). A vanadium–titania phosphate catalyst is employed in that process.

4. Manufacture

Commercial production of acetic acid has been revolutionized in the decade 1978–1988. Butane–naphtha liquid-phase catalytic oxidation has declined precipitously as methanol [67-56-1] or methyl acetate [79-20-9] carbonylation has become the technology of choice in the world market. Most commercial production of virgin synthetic acetic acid is based on methanol carbonylation (1). By-product acetic acid recovery in other hydrocarbon oxidations, eg, in xylene oxidation to terephthalic acid and propylene conversion to acrylic acid, has also grown. Production from synthesis gas is increasing and the development of alternative raw materials is under serious consideration following widespread dislocations in the cost of raw material (see CHEMURGY).

Ethanol fermentation is still used in vinegar production. Research on fermentative routes to glacial acetic acid is also being pursued. Thermophilic, anaerobic microbial fermentations of carbohydrates can be realized at high rates, if practical schemes can be developed for removing acetic acid as fast as it is formed. Under usual conditions, ~5% acid brings the anaerobic reactions to a halt, but continuous separation produces high yields at high production rates. Heat for the reaction is provided by the metabolic activity of the microorganisms. Fermentative condensation of CO_2 is another possible route to acetic acid.

Currently, almost all acetic acid produced commercially comes from acetaldehyde oxidation, methanol or methyl acetate carbonylation, or light hydrocarbon liquid-phase oxidation. Comparatively small amounts are generated by butane liquid-phase oxidation, direct ethanol oxidation, and synthesis gas. Large amounts of acetic acid are recycled industrially in the production of cellulose acetate, poly(vinyl alcohol), aspirin peracetic acid, and in a broad array of other proprietary processes. (These recycling processes are not regarded as production and are not discussed herein.)

4.1. Acetaldehyde Oxidation. Ethanol [64-17-5] is easily dehydrogenated oxidatively to acetaldehyde (qv) using silver, brass, or bronze catalysts. Acetaldehyde can then be oxidized in the liquid phase in the presence of cobalt or manganese salts to yield acetic acid. Peracetic acid [79-21-0] formation is prevented by the transition metal catalysts (8). (Most transition metal salts decompose any peroxides that form, but manganese is uniquely effective.) Kinetic system models are useful for visualizing the industrial operation (32, 33). Stirred-tank and sparger reactor rates have been compared for this reaction and both are so high that they are negligible in the reaction's mathematical description.

Figure 1 is a typical flow sheet for acetaldehyde oxidation. The reactor is an upright vessel, fitted with baffles to redistribute and redirect the air bubbles. Oxygen is fully depleted by the time a bubble reaches the first baffle and bubbles above the first baffle serve mainly for liquid agitation. Such mechanical contacting decomposes transitory intermediates and stabilizes the reactor solution. Even though the oxidizer-reactor operates under mild pressure, sufficient aldehyde boils away to require an off-gas scrubber. Oxidate is passed into a column operated under a positive nitrogen pressure, hence to an acetaldehyde recovery column where unreacted aldehyde is recycled. More importantly, many dangerous peroxides are decomposed in this column, some into acetic acid, while traces of ethanol are esterified to ethyl acetate. Crude acid is taken off at the bottom and led to a column for stripping off the low boiling constituents other than aldehyde.

Crude oxidate is passed to a still where any remaining unreacted acetaldehyde and low boiling by-products, eg, methyl acetate and acetone [67-64-1], are removed as are CO, CO_2, and N_2. High concentration aqueous acetic acid is obtained. The main impurities are ethyl acetate, formaldehyde, and formic acid although sometimes traces of a powerful oxidizing agent, possibly diacetyl peroxide, are present. If the acetaldehyde contains ethylene oxide, then ethylene glycol diacetate is present as an impurity. Formic acid can be entrained using hexane or heptane, ethyl acetate, or a similar azeotroping agent. Often the total contaminant mass is low enough to permit destruction by chemical oxidation. The oxidizing agent, such as sodium dichromate, is fed down the finishing column as a concentrated solution. Potassium permanganate solution is also effective, but it often clogs the plates of the distillation tower.

Final purification is effected by distillation giving high purity acid. Some designs add ethyl acetate to entrain water and formic acid overhead in the finishing column. The acid product is removed as a sidestream. Potassium permanganate has been employed to oxidize formaldehyde and formic acid because the finished acid must pass a permanganate test. The quantity of water in the chemical oxidizer solution is important for regulating the corrosion rate of the finishing column: Acetic acid having a purity of 99.90–100% corrodes stainless steel SS-316 or SS-320. Lowering the acid concentration to 99.75–99.80% with distilled water in the permanganate solution diminishes the corrosion rate dramatically. Residues containing manganese acetate or chromium acetate are washed with a two-phase mixture of water–butyl acetate or water–toluene. The organic solvent removes high boiling materials, tars and residual acid, and the metallic acetates remain in the water layer (34).

Alternative purification treatments have been explored but have no industrial application. Nitric acid or sodium nitrate causes the oxidation of formic acid and formaldehyde, but provokes serious corrosion problems. Schemes have been devised to reduce rather than oxidize the impurities; eg, injecting a current of

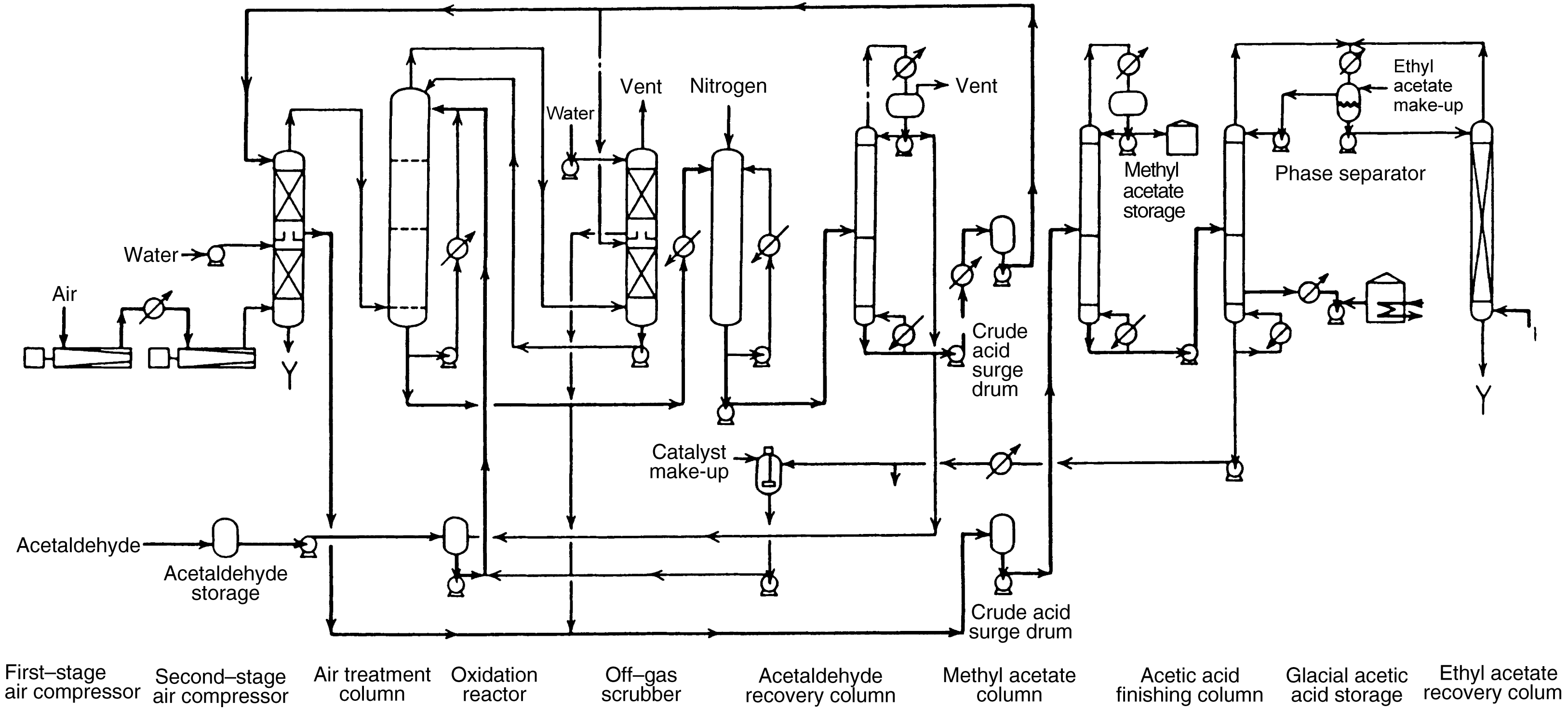

Fig. 1. A typical acetaldehyde oxidation flow sheet.

hydrogen and passing the acid over a metallic catalyst such as nickel or copper turnings. Since reduction occurs at 110–120°C, the reaction can be run in the final column. The risk of an explosion from the hydrogen passing through the column and venting at the top probably discourages the use of this treatment. Certain simple salts, eg, $FeSO_4$ or $MnSO_4$, may be introduced in the same way as the permanganate or dichromate discussed earlier. These serve to eliminate most of the quality-damaging impurities.

Conversion of acetaldehyde is typically >90% and the selectivity to acetic acid is higher than 95%. Stainless steel must be used in constructing the plant. This established process and most of the engineering is well understood. The problems that exist are related to more extensively automating control of the system, notably at start-up and shutdown, although even these matters have been largely solved. This route is the most reliable of acetic acid processes.

4.2. Methanol Carbonylation. Several processes were patented in the 1920s for adding carbon monoxide to methanol to produce acetic acid (35). The earliest reaction systems used phosphoric acid at 300–400°C under high CO pressures. Copper phosphate, hydrated tungstic oxide, iodides, and other materials were tried as catalysts or promoters. Nickel iodide proved to be particularly valuable. At that time, only gold and graphite were recognized as adequate to resist temperatures of 300–320°C and pressures of 20 MPa (2900 psi). In 1945–1946, when German work was disclosed by capture of the Central Research Files at Badische Anilin, a virtually complete plant design became public. Although this high pressure methanol carbonylation system suffered, many of the difficulties experienced in earlier processes, eg, loss of iodine, corrosive conditions, and dangerously high pressures, new alloys such as Hastelloy C permitted the containment of nearly all the practical problems. Experimental and pilot-plant units were operated successfully and, by 1963 BASF opened a large plant at Ludwigshafen, Germany providing license to Borden Chemical Company for a similar unit in Louisiana in 1966.

In 1968, a new methanol carbonylation process using rhodium promoted with iodide as catalyst was introduced by a modest letter (36). This catalyst possessed remarkable activity and selectivity for conversion to acetic acid. Nearly quantitative yields based on methanol were obtained at atmospheric pressure and a plant was built and operated in 1970 at Texas City, Tex. The effect on the world market has been exceptional (37).

Low pressure methanol carbonylation transformed the market because of lower cost raw materials, gentler, lower cost operating conditions, and higher yields. Reaction temperatures were 150–200°C and the reaction was conducted at 3.3–6.6 MPa (33–65 atm). The chief efficiency loss was conversion of carbon monoxide to CO_2 and H_2 through a water–gas shift as shown.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The subject has been reviewed (38, 39). Water may be added to the feed to suppress methyl acetate formation, but is probably not when operating on an industrial scale. Water increase methanol conversion, but it is involved in the unavoidable loss of carbon monoxide. A typical methanol carbonylation flow sheet is given in Figure 2.

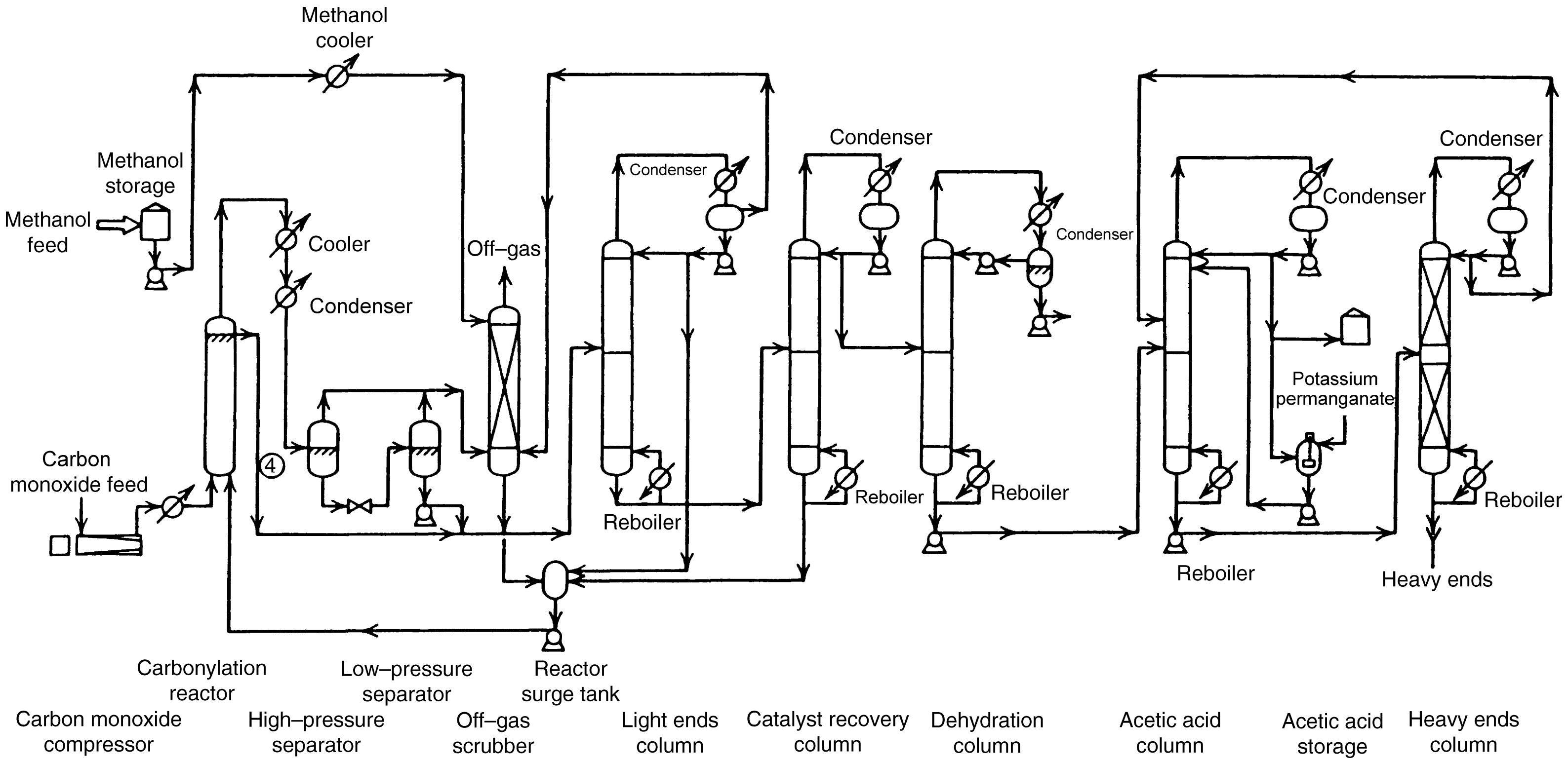

Fig. 2. A typical methanol carbonylation flow sheet.

Low boiling substances are removed from the chilled reactor product by distilling up to a cut point of 80°C. These low boilers are gaseous dimethyl ether, methyl acetate, acetaldehyde, butyraldehyde, and ethyl acetate. The bottoms are flash distilled to recover the rhodium catalyst. Flash distilled acid is azeotropically dehydrated. In the final distillation, glacial acid is obtained. Traces of iodine that may remain in the finished acid may be removed by fractional crystallization or by addition of a trace of methanol followed by distillation of the methyl iodide that forms. Somewhere in the carbonylation reaction, a minute amount of propionic acid seems to be made. It typically is found in the residues of the acetic acid finishing system and can be removed by purging the finishing column bottoms.

Vapor-phase methanol carbonylation over a supported metal catalyst has been described (40, 41). Methanol itself is obtained from synthesis gas, so the possibility of making acetic acid directly without isolating methanol has been explored (42) in both vapor and liquid phases. Alcohols are generated from CO and H_2 using halide promoted ruthenium, but acetic acid can be produced by addition of $Ru_3(CO)_{12}$ (43). A complex metallic catalyst containing rhodium, manganese, iridium, and lithium supported on silica has been used to provide selective synthesis (44). Ruthenium melt catalyst has been patented (45). Catalysts can be improved by running them in by stages to the optimum operating temperature over prolonged time periods, eg, 100–1000 h (46). A rhodium–nickel–silver catalyst for this reaction has been developed (47). An iridium catalyzed carbonylation process for the production of acetic acid has been patented (48).

Synthesis gas is obtained either from methane reforming or from coal gasification (see COAL CONVERSION PROCESSES). Telescoping the methanol carbonylation into an esterification scheme furnishes methyl acetate directly. Thermal decomposition of methyl acetate yields carbon and acetic anhydride,

$$2\,CH_3COCH_3 \longrightarrow (CH_3CO)_2O + C(\text{soot})$$

but a pyrolytic route is not attractive because of excessive energy consumption. Methyl acetate carbonylation yields both anhydride and acetic acid, controllable in part by the conditions. A plant based on this process was put in operation in October 1983 (49).

4.3. Butane–Naphtha Catalytic Liquid-Phase Oxidation.

Direct liquid-phase oxidation of butane and/or naphtha [8030-30-6] was once the most favored worldwide route to acetic acid because of the low cost of these hydrocarbons. Butane [106-97-8], in the presence of metallic ions, eg, cobalt, chromium, or manganese, undergoes simple air oxidation in acetic acid solvent (50). The peroxidic intermediates are decomposed by high temperature, by mechanical agitation, and by action of the metallic catalysts, to form acetic acid and a comparatively small suite of other compounds (51). Ethyl acetate and butanone are produced, and the process can be altered to provide larger quantities of these valuable materials. Ethanol is thought to be an important intermediate (52); acetone forms through a minor pathway from isobutane present in the hydrocarbon feed. Formic acid, propionic acid, and minor quantities of butyric acid are also formed.

The theoretical explanation of the butane reaction mechanism is as fully developed as is that of acetaldehyde oxidation (53). The theory of the naphtha oxidation reaction is more troublesome, however, and less well understood, largely because of a back-biting reaction that leads to cyclic products (54).

Liquid-phase butane oxidation is realized in a sparged column, fabricated of high alloy stainless steel. Cobalt, chromium, and manganese acetate catalyst is dissolved in acetic acid and introduced with the butane–acetic acid solution. Air or O_2-enriched air may be used. The temperature is kept just below the critical temperature of butane, 152°C. Pressure is ~5.6 MPa (812 psi) (55). The reactor product is cooled and the pressure slowly lowered. In stripping the low boiling constituents away from the reactor product, the first obtained is unreacted butane, which is often led through an expansion turbine that powers air compressors for the reactor and cools the product. The butane is then recycled to the reactor. After cooling, the reactor oxidate appears as two phases: a hydrocarbon-rich phase and a denser aqueous phase. The former is decanted and led back into the reactor; the latter is distilled to obtain the boiling oxygenates. Butanone [78-93-3] and ethyl acetate [141-78-6] are the chief constituents of the aqueous layer, but there are traces of methyl vinyl ketone (an unpleasant lacrimator), aldehydes, and esters. Formic acid, also present, forms a maximum-boiling azeotrope that boils higher than either of the chief constituents.

Although acetic acid and water are not believed to form an azeotrope, acetic acid is hard to separate from aqueous mixtures. Because a number of common hydrocarbons such as heptane or isooctane form azeotropes with formic acid, one of these hydrocarbons can be added to the reactor oxidate permitting separation of formic acid. Water is decanted in a separator from the condensate. Much greater quantities of formic acid are produced from naphtha than from butane, hence formic acid recovery is more extensive in such plants. Through judicious recycling of the less desirable oxygenates, nearly all major impurities can be oxidized to acetic acid. Final acetic acid purification follows much the same treatments as are used in acetaldehyde oxidation. Acid quality equivalent to the best analytical grade can be produced in tank car quantities without difficulties.

Two explosions, on November 14, 1987, at the largest butane liquid-phase oxidation plant resulted in 3 deaths and 37 people injured (56). The plant, which had operated since December 1952 free of such disasters, was rebuilt (57).

4.4. Prospective Processes. There has been much effort invested in examining routes to acetic acid by olefin oxidation or from ethylene, butenes, or *sec*-butyl acetate. Showa Denko brought a 100×10^3 t/year plant on stream based on direct oxidation of ethylene in 1997 (58). A process for a one-step gas-phase production of acetic acid from ethylene (59) from ethane (60), and a process from ethane–ethylene have been described (61).

Recovery of acid from wood distillate has long been viewed as a desirable prospect. Nearly all common lumber woods can be destructively distilled to furnish pyroligneous acid containing ~5–8% acetic acid. Coupled with azeotropic or extractive distillation, good quality glacial acetic acid could be prepared (62, 63). Indeed, glacial acetic acid used to be prepared from gray acetate of lime, formed by the reaction of pyroligneous acid and limestone, by reaction of the acetate with bicarbonate followed by sulfuric acid:

$$Ca(CH_3COO)_2{+}Na_2CO_3 \longrightarrow 2\,Na(CH_3COO) + CaCO_3$$

$$NaOOCCH_3 + H_2SO_4 \longrightarrow NaHSO_4 + CH_3COOH$$

The acetic acid was distilled to give soda acetic acid and upon further purification, it was often used for food or pharmaceutical applications.

Mixtures of trioctylamine and 2-ethylhexanol have been employed to extract 1–9% by volume acetic acid from its aqueous solutions. Reverse osmosis for acid separation has been patented and solvent membranes for concentrating acetic acid have been described (64, 65). Decalin and trioctylphosphine were selected as solvents (66). Liquid–liquid interfacial kinetics is an especially significant factor in such extractions (67).

The fermentative fixing of CO_2 and water to acetic acid by a species of acetobacterium has been patented; acetyl coenzyme A is the primary reduction product (68). Different species of clostridia have also been used. Pseudomonads (69) have been patented for the fermentation of certain C_1 compounds and their derivatives, eg, methyl formate. These methods have been reviewed (70). The manufacture of acetic acid from CO_2 and its dewatering and refining to glacial acid has been discussed (71, 72).

The autotropic pathway for acetate synthesis among the acetogenic bacteria has been examined (73). Quantitative fermentation of 1 mol of glucose [50-99-7], $C_6H_{12}O_6$, yields 3 mol of acetic acid, while 2 mole of xylose [58-86-6], $C_5H_{10}O_5$, yields 5 mole. The glucose reaction is

$$C_6H_{12}O_6 + 2\,H_2O \longrightarrow 2\,CH_3COOH + 2\,CO_2 + 8\,H^+ + 8\,e^-$$

$$2\,CO_2 + 8\,H^+ + 8\,e^- \longrightarrow CH_3COOH + 2\,H_2O$$

Simply by passing gaseous H_2–CO_2 through an aqueous sugar mixture, the carbon dioxide is fixed into acetic acid:

$$2\,CO_2 + 4\,H_2 \longrightarrow CH_3COOH + 2\,H_2O$$

Using carbon monoxide, the reaction becomes

$$4\,CO + 2\,H_2O \longrightarrow CH_3COOH + 2\,CO_2$$

A number of C_1 compounds act as surrogates for reduction. A microbial process for the preparation of acetic acid as well as solvent for its extraction from the fermentation broth has been patented (74).

The possibility of using fermentation to generate a safe, noncorrosive road deicing composition has been studied (75). Calcium magnesium acetate [76123-46-1] is readily prepared from low concentration acetic acid produced from glucose or other inexpensive sugars. The U.S. Federal Highway Administration has financed development of anaerobic, thermophilic bacteria in an industrial process to manufacture calcium magnesium acetate from hydrolyzed corn starch and dolime [50933-69-2]. It is equally possible to utilize CH_3OH–CO_2 or H_2–CO_2 mixtures. These fermentative processes lead to dilute acid, often no more than 5 wt%, so that a concentration procedure is essential to recovery. Another new method for acetic acid production is electrodialytic conversion of dilute sodium acetate into concentrated acid (76). Electrodialytic fermentation systems have been subjected to computerized control and the energy cost for recovery is rapidly being diminished.

5. Shipping and Handling

Acetic acid, providing the concentration is greater than 99%, may be stored and shipped in aluminum. Aluminum slowly corrodes forming a layer of basic aluminum acetate that prevents further corrosion. Some of this basic oxide coating is suspended in the acid and the heels of tank cars often have a white or gray, cloudy appearance. Water increases the corrosion rate significantly; hence every effort must be devoted to maintaining a high acid concentration. Mercury in minute quantities catalyzes corrosion of aluminum by acetic acid so that a single broken thermometer can provoke catastrophic and dangerous corrosion in 99.6–99.7% glacial acid. Mercurial thermometers are often absolutely prohibited near aluminium tank cars or barrels. Acid can also be stored and shipped in stainless steel, glass carboys, and polyethylene drums.

Because glacial acetic acid freezes at $\sim 16\,^{\circ}\mathrm{C}$, exceptional care must be taken for melting the product in cool weather. Electrical or steam heaters may be employed. Tank cars or tank wagons must be fitted with heating coils, which can be attached to a steam line and trap. Tank vents must be traced with electrical or steam lines to prevent crystallization. Acetic acid sublimes so that a single, large crystal can appear and completely fill an otherwise adequate vent.

According to the U.S. DOT regulations, acetic acid is a corrosive material (77). It may be shipped in metal or plastic packaging when no more than 0.45 kg is involved. Greater quantities may be shipped in boxed glass carboys, kegs or plywood drums, wooden barrels lined with asphalt or paraffin, earthenware containers in protective boxes, or plastic drums. It may not be shipped in plastic bags. Steel drums having polyethylene liners or polyethylene drums having steel overpacks are acceptable. Polyethylene drums do not appear to cause trace contamination after 12-months storage. Nonreturnable containers ought to be emptied and rinsed with fresh water. No other chemical ought to be shipped or stored in acetic acid containers.

Tank wagons are used for acetic acid deliveries in amounts intermediate between drum and tank car shipments, or to destinations not served by railways. Tank wagons are usually fabricated of stainless steel or aluminum alloy. Most shipments are carried in railway tank cars with nominal capacities of 38–76 m^3 (10,000–20,000 gal). For bookkeeping, capacities are determined by weight instead of volume measurements. Some tank cars are unloaded by suction, others by applying a positive nitrogen pressure and then siphoning the acetic acid into an education tube. Siphoning is frequently required by local laws.

Acetic acid is also transported in barges, sometimes in amounts of 1500–1750 tons. Acetic acid is not as hygroscopic as some other anhydrous organic substances, but barge shipments occasionally have specification problems because of wave splashing into the tanks or other careless handling.

6. Economic Aspects

Acetic acid has a place in organic processes comparable to sulfuric acid in the mineral chemical industries and its movements mirror the industry. Growth of synthetic acetic acid production in the United States was greatly affected by the

Table 7. **North American Producers of Acetic Acid and Their Capacities**[a]

Producer	Capacity × 10^3 t (×10^6 lb)/year
Virgin acid	
Celanese, Clear Lake, Tex.	998 (2,200)
Celanese, Pampa, Tex.	267 (590)
Eastman, Kingsport, Tenn.	254 (560)
Millennium, LaPorte, Tex.	453 (1000)
Sterling, Texas City, Tex.	453 (1000)
Total	*2,425 (5,350)*
Recovered Acid	
Air Products, Calvert City, Ky.	57 (125)
Air Products, Pasadena, Tex.	36 (80)
Celanese, Narrows, Va.	150 (330)
Celanese, Rock Hill, S.C.	150 (330)
DuPont, LaPorte, Tex.	82 (180)
Eastman, Kingsport, Tenn.	284 (625)
Primester, Kingsport, Tenn.	73 (160)
Other, small producers (9 locations)	98 (215)
Total	*930 (2045)*
U.S. Total	*3,355 (7395)*
Virgin Acid	
Celanese Canada, Edmonton, Alberta	91 (200)
Industrias Monfel, San Luis Potosi, Mexico	26 (45)
Total	*111 (245)*
Recovered Acid	
Celanese Canada, Edmonton, Alberta	36 (80)
Total	*36 (80)*
Other North American Total	*147 (325)*
Total	*3502 7720*

[a] Ref. 1, as of Feb. 26, 2001.

dislocations in fuel resources of the 1970s. The growth rate for 1994–1999 was 26% with an estimate of 2.6% through 2003.

North American producers and their capacities as of Feb. 2001 are listed in Table 7 (1).

Most commercial production of virgin acetic acid is based on methanol carbonylation. Celanese produces acetic acid by the liquid-phase oxidation of *n*-butane.

World producers of acetic acid and their production are listed in Table 8 (58)

Major customers for acetic acid are listed below (58).

United States: Amoco Chemical, DuPont, Union Carbide.

Europe: Elf Atochem, DuPont, Courtaulds Fibres.

Asia/Pacific: Kohap Petrochemical, Samnam Petrochemical, Samsung Petrochemical, Capco, Dupont.

Historical prices for acetic acid for 1995–2000 was a high of \$0.36/lb tech. tank, delivered, E., and a low of \$0.23/lb, same basis. Prices in of Feb. 2001 were from \$0.44 to \$0.47/lb.

Table 8. **Other International Producers of Acetic Acid and Their Capacities**

Producer	Capacity $\times 10^3$ t
South America	38
Western Europe	
U.K.	
BP Chemicals, Hull	675
France	
Acetex, Pardies	400
Germany	
Celanese Chemical, Frankfurt	180
Hurth-Knapsack	70
Wacker-Chemie, Burghausen	80
BASF, Ludwigshafen	50
Switzerland	
Lonza, Visp	30
Eastern Europe	207
Asia Pacific	
China	795
Japan	
Kyodo Sakussan, Himeji, Hyogo	400
Showa Denko, Oita	250
Daicel, Otake	36
Korea	
Samsung-BP Chemical, Ulsan	350
India	230
Taiwan	
China Petrochemical Development, Ta-sheh Hsian	100
Chang Chun Petrochemical, Miaoli City	60
Indonesia	
Indo Acidtama, Solo	33

7. Specifications and Analysis

Most specifications and analytical methods have been given (78). Most of the standards have remained unchanged for the past half-century. They were designed for acid recovered from wood tar condensates. All acid of commerce easily passes these tests.

Acetic acid made by methanol carbonylation sometimes has traces of iodine or bromine if the acid comes from the high pressure route. Qualitatively, these may be quickly detected by the Beilstein test for halogens: A copper wire is heated in a gas burner until no color can be seen and the coil plunged into the acetic acid, then brought into the gas flame again. Any trace of green or blue-green flame shows the presence of halogen. The lower identification threshold is ~0.7 ppm for chloride, ~0.65 ppm for bromide, and ~0.55 for iodide.

Super-pure acid is often specified by performance tests. Acetic acid to be used for Wijs Reagent must be very highly purified, otherwise the reagent deteriorates quickly. The dichromate–sulfuric acid test, made by dissolving potassium dichromate in concentrated H_2SO_4, and then mixing with an equal volume of acetic acid, is a sensitive test for minute quantities of certain oxidizing agents. These substances can be removed only by such special treatments as refluxing the acid with dichromate or permanganate, followed by redistillation. In commercial practice, instrumental methods are used to monitor quality but these methods are seldom given officially as standards. Gas chromatographic and mass spectrometric methods are capable of very high sensitivity.

Glacial acetic acid is considered to be 99.50 wt % or higher. A different grade has a minimum concentration of 99.70 wt %. Specialty users require water solutions of 86 and 36%. Such grades are prepared on special order. Only minor quantities of these grades are marketed, and their use is vanishing.

8. Health and Safety Factors

Acetic acid has a sharp odor and the glacial acid has a fiery taste and will penetrate unbroken skin to make blisters. Prolonged exposure to air containing 5–10 mg/m^3 does not seem to be seriously harmful, but there are pronounced, undesirable effects from constant exposure to as high as 26 mg/m^3 over a 10-day period (9).

Humans exude ~90 mg/day of volatile fatty acids in exhaled breath and perspiration, 80% of which is acetic acid (74). In a confined environment, as much as 15–20 mg/m^3 can accumulate and such concentrations can become serious in submarines or space capsules.

Concentrated aqueous or organic solutions can be strongly damaging to skin. Any solution containing >50% acetic acid should be considered a corrosive acid. Acetic acid can irreparably scar delicate tissues of the eyes, nose, or mouth. The acid penetrates the mucosa of the tongue that is near the pK of the acid (88). The action of acetic acid is insidious. There is no quick burning sensation when applied to the unbroken skin. Blisters appear within 30 min to 4 h. Little or no pain is experienced at first but when sensory nerve receptors are attacked, severe and unremitting pain results. Once blistering occurs, washing with water or bicarbonate seldom relieves the pain. Medical care should be sought immediately.

Care ought to be taken in handling acetic acid to avoid spillage or otherwise breathing vapors. Wash any exposed areas with large amounts of water. Once the odor of acetic acid vapors is noticeable, the area should be abandoned

Table 9. **United States and International Standards for Acetic Acid**[a]

Country	Exposure limits
U.S. OSHA PEL	TWA 10 ppm (25 mg/m^3)
U.S. NIOSH REL	TWA 10 ppm (25 mg/m^3) STEL/CEIL (C) 15 ppm (37 mg/m^3)
U.S. ACGIH TLV	TWA 10 ppm (25 mg/m^3) STEL/CEIL (C) 15 ppm (37 mg/m^3)
Australia	TWA 10 ppm (25 mg/m^3); STEL/CEIL (C) 15 ppm (37 mg/m^3)
Austria	TWA 10 ppm (25 mg/m^3)
Belgium	TWA 10 ppm (25 mg/m^3); STEL 15 ppm (37 mg/m^3)
Czechoslovakia	TWA 25 mg/m^3; STEL 15 ppm (37 mg/m^3)
Denmark	TWA 10 ppm (25 mg/m^3)
Finland	TWA 10 ppm (25 mg/m^3); STEL 15 ppm (37 mg/m^3)
France	STEL 10 ppm (25 mg/m^3)
Germany (DFG MAK)	TWA 10 ppm (25 mg/m^3)
Hungary	TWA 10 mg/m^3; STEL 20 mg/m^3
India	TWA 10 ppm (25 mg/m^3); STEL 15 ppm (37 mg/m^3)
Ireland	TWA 10 ppm (25 mg/m^3); STEL 15 (37 mg/m^3)
Japan (JSOH)	TWA 10 ppm (25 mg/m^3)
The Netherlands	TWA 10 ppm (25 mg/m^3)
The Philippines	TWA 10 ppm (25 mg/m^3)
Poland	TWA 15 mg/m^3; STEL 30 mg/m^3
Russia	TWA 10 ppm; STEL 5 mg/m^3, skin
Sweden	TWA 10 ppm (25 mg/m^3); STEL 15 ppm (35 mg/m^3)
Switzerland	TWA 10 ppm (25 mg/m^3); STEL 20 ppm (50 mg/m^3)
Thailand	TWA 10 ppm (25 mg/m^3)
Turkey	TWA 10 ppm (25 mg/m^3)
United Kingdom (HSE OES)	TWA 10 ppm (25 mg/m^3) STEL/CEIL (C) 15 ppm (37 mg/m^3)

[a] Ref. 81

immediately. Table 9 gives U.S. and international exposure limits for acetic acid (58).

Glacial acetic acid is dangerous, but its precise toxic dose is not known for humans. The LD_{50} for rats is said to be 3310 mg/kg, and for rabbits 1200 mg/kg (82). Ingestion of 80–90 g must be considered extraordinarily dangerous for humans. Vinegar, on the other hand, which is dilute acetic acid, has been used in foods and beverages since the most ancient of times. Although vinegar is subject to excise taxation in many countries of the world other than the United States, acetic acid for nonfood applications is commonly exempted (83).

Industrial plants for acetic acid production sometimes have waste streams containing formic and acetic acid. The quantity of acids in these streams is not significant to the overall plant efficiency, but from a safety viewpoint such material must either be recycled, treated with alkaline substances, or consumed microbially. Recycling is probably the most expensive route because the cost of processing is not repaid by an increase in efficiency. In Europe, these streams must be neutralized or degraded biologically. In Germany, no more than 3 kg/h may be emitted in vent gases, with a maximum of 150 mg/m^3 (83). The acid must be removed from the vent gas by scrubbing or chilling.

9. Uses

The uses for acetic acid are as follows: 41% is used in the production of vinyl acetate, 36% for the production of cellulose acetate and acetic anhydride, 11% for the production of acetate esters. 7% for the production of terephthalic acid, 5% miscellaneous including textiles and chloroacetic acid.

Acetic acid is used as solvent for the production of terephthalic acid. This use is growing at the rate of 6.5% per year because of the demand for terephthalic acid in the production of poly(ethylene trephthalate) resins.

Some uses for acetic acid described in recent patent applications include the following: as a signal enhancing agent in fluorescence spectroscopy (84); in the production of fruit vinegar from citrus juice (85); in a dilute cleaning composition for use in semiconductor fabrication (86); in a formulation used to control diseases in beehives (87); and in etching a substrate (88).

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