

Acetic Acid

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1. Introduction

Acetic acid [64-19-7], CH₃COOH, *M_r* 60.05, is found in dilute solutions in many plant and animal systems. Vinegar, an aqueous solution containing about 4–12% acetic acid, is produced by the fermentation of wine and has been known for more than 5000 years.

The major producers of acetic acid, accounting for ca. 70% of total worldwide production, are the United States, Western Europe, and Japan. World capacity exceeds 7×10^6 t/a [1]. The largest end uses are in the manufacture of vinyl acetate [108-05-4] and acetic anhydride [108-24-7]. Vinyl acetate is used in the production of latex emulsion resins for applications in paints, adhesives, paper coatings, and textile treatment. Acetic anhydride is used in the manufacture of cellulose acetate textile fibers, cigarette filter tow, and cellulose plastics.

2. Physical Properties

Acetic acid is a clear, colorless, corrosive liquid that has a pungent odor and is a dangerous vesicant. It has a *pK_a* of 4.77 [2]. It melts at 16.75 °C [3] and boils at 117.9 °C [4] under 101.3 kPa [5]. It has a pungent vinegarlike odor. The detectable odor is as low as 1 ppm. The acid is combustible with a low flash point of 43 °C. The explosion limits of acetic acid vary from the upper explosion limit (UEL) of 16% at 92 °C to the lower explosion limit (LEL) of 4% at 59 °C. The liquid is usually available as glacial acetic acid with less than 1 wt% water and over 98% purity. Besides water, the acid contains traces of impurities such as acetaldehyde, oxidized substances, iron, and chlorides.

Occasionally, the acid may be colored due to the presence of ethyl acetoacetate [141-97-9]. The acetate is easily mistaken for formic acid

Table 1. Freezing points for various acetic acid – water mixtures

wt % CH ₃ COOH	<i>fp.</i> °C	wt % CH ₃ COOH	<i>fp.</i> °C
100	16.75	96.8	11.48
99.6	15.84	96.4	10.83
99.2	15.12	96.0	10.17
98.8	14.49	93.5	7.1
98.4	13.86	80.6	– 7.4
98.0	13.25	50.6	–19.8
97.6	12.66	18.1	– 6.3
97.2	12.09		

Table 2. Densities of aqueous acetic acid solutions at 15 °C

wt % CH ₃ COOH	ρ , g/cm ³	wt % CH ₃ COOH	ρ , g/cm ³
1	1.007	60	1.0685
5	1.0067	70	1.0733
10	1.0142	80	1.0748
15	1.0214	90	1.0713
20	1.0284	95	1.0660
30	1.0412	97	1.0625
40	1.0523	99	1.0580
50	1.0615	100	1.0550

because it reduces mercuric chloride. Traces of mercury may cause extensive corrosion by reaction with aluminum. Aluminum is a common material for containers to ship the acid [6].

Glacial acetic acid is very hygroscopic. The presence of 0.1 wt % water lowers the freezing point significantly [7]. Measuring the freezing point is a convenient way to evaluate acetic acid purity. This is shown in Table 1 [8].

Acetic acid forms azeotropes with many common solvents, such as benzene, pyridine, and dioxane. Acetic acid is miscible with water, ethanol, acetone, benzene, ether, and carbon tetrachloride. However, it is not soluble in CS₂ [2].

The physical properties of acetic acid are well documented, and their accuracy is important for commercial production. For instance, design and operation of distillation processes requires precise data. High-precision values provide a valuable asset to the chemical industry [9, 10].

The density of mixtures of acetic acid and water [11–13] is listed in Table 2. The density exhibits a maximum between 67 wt % and 87 wt %, corresponding to the monohydrate (77 wt % acetic acid). The density of pure acetic acid as a function of temperature is listed in Table 3 [14, 15].

Due to the difficulty in eliminating traces of water from acetic acid, the value for the boiling point varies from 391 to 392 K [10]. Careful studies prove that pure acetic acid boils at 391.10 K under 101.325 kPa [16]. The critical temperature and critical pressure are 594.45 K and 5785.7 kPa [3].

Precise data on vapor pressure of acetic acid are available from a regression equation (Eq. 1) [10], which covers the range from the normal boiling point to the critical point.

Table 3. Dependence of the density of pure acetic acid on temperature

<i>t</i> , °C	ρ , g/cm ³	<i>t</i> , °C	ρ , g/cm ³
20	1.0491	130	0.9235
26	1.0420	139	0.9119
34	1.0324	140	0.9092
52	1.0134	145	0.9030
60	1.0060	156	0.8889
63	1.0007	180	0.8555
75	0.9875	220	0.7941
85	0.9761	260	0.7136
97	0.9611	300	0.5950
100	0.9599	320	0.4615
107	0.9506	321	0.3506
117	0.9391		

$$P = P_c \exp \left(A + B/T_r + C \ln T_r + DT_r^6 \right) \quad (1)$$

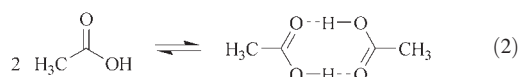
where P is vapor pressure in kPa; T_r is reduced temperature T/T_c , T is temperature in K; T_c is 594.45 K, P_c is 5785.7 kPa, A is 10.08590, B is -10.37932 ; C is -3.87306 , and D is 0.29342.

The vapor pressure of pure acetic acid is given in Table 4 [17]. The density of the vapor corresponds to approximately twice the molecular mass because of vapor-phase hydrogen bonding

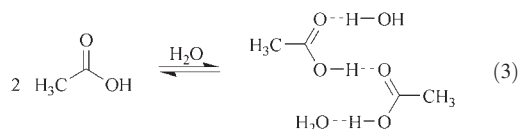
Table 4. Vapor pressure of pure acetic acid

<i>t</i> , °C	<i>p</i> , mbar	<i>t</i> , °C	<i>p</i> , mbar
0	4.7	150.0	2 461.1
10	8.5	160	3 160
20	15.7	170	4 041
30	26.5	180	5 091
40	45.3	190	6 333
50	74.9	200	7 813
60	117.7	210	9 612
70	182.8	220	11 733
80	269.4	230	14 249
90	390.4	240	17 057
100	555.3	250	20 210
110	776.7	260	23 854
118.2	1013	270	28 077
130.0	1386.5	280	32 801
140.0	1841.1		

[8]. Hydrogen-bonded dimers and tetramers have both been proposed. Reports indicate that in the gas phase, the acid exists mainly in an equilibrium between monomer and dimer (Eq. 2) according to vapor density data [18, 19] molecular modeling, IR analysis [20], and gas-phase electron diffraction [21].



In the gas phase, monomeric and dimeric acetic acid undergo extensive hydrolysis [22, 23]. In the liquid state, acetic acid equilibrates between monomer and dihydrated dimer or cyclic dimer (Eqs. 2 and 3) [24]. As the concentration of acetic acid increases, the equilibrium shifts to the right, favoring dimeric acetic acid. As the temperature is increased, the system shifts to the left, favoring the monomer. In addition, the acid may also form open-chain trimers and higher oligomers. However, at about 95 wt %, the acid exists mainly as a cyclic dimer and is no longer associated with water.



Up to 32 wt %, mixing acetic acid with water leads to evolution of heat. At higher acid concentrations heat is absorbed [25]. The measured values of the heat of mixing are consistent with the calculated values based on the dimers and tetramers described above. The aqueous mixture of acetic acid forms a eutectic mixture at -26°C . This eutectic mixture prevented earlier attempts to concentrate the acid by freezing. A way to obtain pure acid is to add urea or potassium acetate to the acid. Then, glacial acetic acid can be distilled.

Other physical properties of acetic acid are listed below.

Specific heat capacity	
Gaseous acid, c_p	1.110 J g ⁻¹ K ⁻¹ at 25 °C [33]
Liquid acid, c_p	2.043 J g ⁻¹ K ⁻¹ at 19.4 °C
Crystalline acid, c_p	1.470 J g ⁻¹ K ⁻¹ at 1.5 °C
	0.783 J g ⁻¹ K ⁻¹ at -175.8°C
Heat of fusion	195.5 J/g [29]

Heat of combustion	-874.2 kJ/mol at 20 °C [30]
Cryoscopic constant	-269.56°C [30]
Ebullioscopic constant	270.62°C [30]
Melting point	6.76°C [31]
Triple-point temperature	16.93°C [19]
Boiling point	118.0°C at 101.3 kPa [32]
Density	1265.85 kg/m^3 (solid at <i>mp</i>)
Viscosity	$11.83 \text{ mPa}\cdot\text{s}$ at 20 °C [26]
	$10.97 \text{ mPa}\cdot\text{s}$ at 25 °C [27]
	$8.18 \text{ mPa}\cdot\text{s}$ at 40 °C [26]
	$0.067 \text{ mPa}\cdot\text{s}$ at critical point [28]
Dielectric constant	6.194 at 20 °C [30]
Dipole moment	$5.804 \times 10^{-30} \text{ C}\cdot\text{m}$ [34]
Electrolyte conductivity	112.0 pS/m [33]
Refractive index n_D^{20}	1.372 [33]
Enthalpy of formation	
ΔH^0 (l, 25 °C)	-484.50 kJ/mol [35]
ΔH^0 (g, 25 °C)	-432.25 kJ/mol
Normal entropy	
S° (l, 25 °C)	$159.8 \text{ J mol}^{-1} \text{ K}^{-1}$ [35]
S° (g, 25 °C)	$282.5 \text{ J mol}^{-1} \text{ K}^{-1}$
Flash point	43°C (closed cup) [36]
	57°C (open cup)
Autoignition point	465°C [36]
Flammability	4.0 to 16.0 vol % in air [36]
Critical data	
p_c	5.786 MPa [3]
T_c	321.45°C [3]

3. Chemical Properties

Many useful materials are made from acetic acid; several are discussed in Chapter 9. Acetate esters are formed by reaction of olefins or alcohols with acetic acid [37]. Acetamide is prepared by the thermal decomposition of ammonium acetate. Acetic acid can be converted to acetyl chloride with phosphorous trichloride or thionyl chloride.

Acetic acid is a raw material for a number of commercial processes. It can be converted to vinyl acetate with ethylene and oxygen (\rightarrow Vinyl Esters). Acetic acid is used in the manufacture of acetic anhydride (\rightarrow Acetic Anhydride and Mixed Fatty Acid Anhydrides) via ketene and in the production of chloroacetic acid (\rightarrow Chloroacetic Acids) using chlorine.

4. Production

Vinegar is still made by fermentation (\rightarrow Vinegar). However, the most important synthetic routes to acetic acid are methanol carbonylation and liquid-phase oxidation of butane, naphtha, or acetaldehyde. Methanol carbonylation has been

the method of choice for the past 25 years [38–40] and will likely remain the preferred route for large-scale production.

Several new technologies for producing acetic acid are being studied. Showa Denko may produce acetic acid by the gas-phase reaction of ethylene with oxygen over a supported palladium catalyst that contains a heteropolyacid or salt [41]. Numerous patents and publications discuss the production of acetic acid directly from ethane and oxygen. Production of acetic acid and acetate salts by microorganisms has also received considerable attention.

4.1. Carbonylation of Methanol

The manufacture of acetic acid from methanol [67-56-1] and carbon monoxide [630-08-0] at high temperature and high pressure was described by BASF as early as 1913 [42].



In 1941 REPPE at BASF demonstrated the efficiency of group VIII metal carbonyls as catalysts for carbonylation reactions, including hydroformylation [43, 44]. This led to the development of a high-pressure, high-temperature process (700 bar, 250 °C) with a cobalt iodide catalyst. The thrust of this work was to develop an acetic acid process not dependent on petroleum-based feedstocks. The current advantage of the methanol carbonylation route to acetic acid is the favorable raw material and energy costs. The synthesis gas raw material required for this process can be obtained from a variety of sources, which range from natural gas to coal. The cobalt-based carbonylation process was commercialized in 1960 by BASF in Ludwigshafen, Federal Republic of Germany [43, 45–47]. The initial capacity of 3600 t/a was expanded to 45 000 t/a by 1981 [48]. In 1966 Borden Chemical Co. started up a 45 000 t/a acetic acid unit in Geismar, Louisiana, United States, based on the BASF technology [43, 45]. The unit was expanded to 64 000 t/a by 1981 before it was shut down in 1982 [1, 48]. This unit was brought on stream again in 1988 for one year to meet acetic acid supply shortages in the United States.

Monsanto developed a low-pressure acetic acid process in the late 1960s with a rhodium iodide promoted catalyst system that demonstrat-

ed significantly higher activity and selectivity than the cobalt-based process. Methanol can be carbonylated even at atmospheric pressure with yields of 99 % and 90 % with respect to methanol and carbon monoxide, respectively [49]. This process was proven commercially in 1970 at Texas City, Texas. The initial plant capacity of 135 000 t/a has been expanded to 270 000 t/a since 1975 [1]. Operating conditions in the reactor are much milder (3 MPa and 180 °C) than in the BASF process [50]. Soon after the Monsanto process was commercialized, the BASF process became uncompetitive, so the Monsanto process is the preferred technology for grass-roots acetic acid units. Since the start-up of the Texas City plant by Monsanto, more than ten companies have licensed and operated this technology worldwide.

In 1978 at the Clear Lake Texas Plant, Celanese Chemical Company (now Celanese, Ltd.) was the first licensee to demonstrate commercially the rhodium-catalyzed Monsanto process. Initial capacity was 27 000 t/a [51]. In the early 1980s, Celanese developed a proprietary low-reaction-water rhodium-catalyzed methanol carbonylation process by modification of the original Monsanto high-reaction-water chemistry. Modifications to the catalyst system by the addition of inorganic iodide salts improved catalyst stability and activity significantly [52]. This technology improvement enabled the Clear Lake unit to expand by more than three times the original capacity to 900 000 t/a with minor capital cost [53].

In 1986, BP Chemicals purchased from Monsanto the high-reaction-water, low-pressure, rhodium-catalyzed methanol carbonylation technology and licensing rights. The acquisition of the technology did not include the improvements developed by Celanese Chemical Company.

Monsanto in the early 1960s also discovered that iridium, like rhodium, is an effective methanol carbonylation catalyst. This catalyst system has since been developed commercially by BP in the early 1990s and is known as the Cativa process [54]. This process was utilized to convert the original rhodium-catalyzed methanol carbonylation plant in Texas City to an iridium-based process. Several advantages claimed by BP for the Cativa process over the conventional rhodium-catalyzed high reaction water carbonylation process include superior catalyst stability, oper-

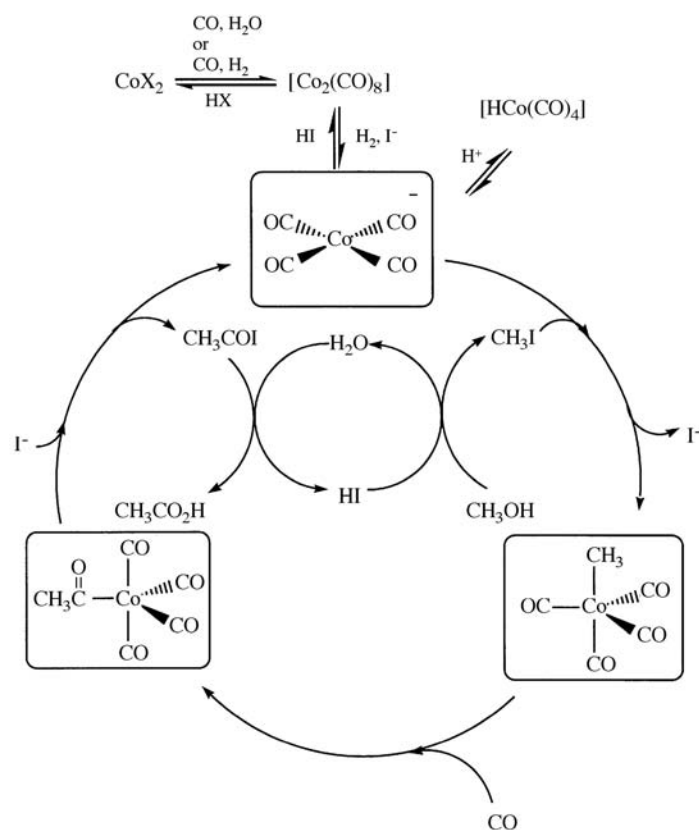


Figure 1. Reaction cycle proposed for the cobalt-catalyzed methanol carbonylation reaction (BASF process)

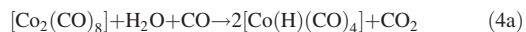
ation at lower reaction water, and less liquid byproducts [55].

Chemistry and Reaction Conditions. The chemistry of the cobalt- (BASF), rhodium- (Monsanto and Celanese), and iridium-catalyzed (BP) processes is similar in requiring promotion by iodide, but the different kinetics indicate different rate-determining steps. In all three processes, two important catalytic cycles are common, one that involves the metal carbonyl catalyst and one that involves the iodide promoter [56, 57].

The cobalt-catalyzed *BASF process* uses cobalt(II) iodide [15238-00-3] for in situ generation of $[\text{Co}_2(\text{CO})_8]$ and hydrogen iodide [10034-85-2]. Compared to other methanol carbonylation processes, severe conditions are required to give commercially acceptable reaction rates. The rate of reaction depends strongly on both the partial pressure of carbon monoxide and the methanol

concentration. Acetic acid yields are 90% based on methanol and 70% based on carbon monoxide. A proposed mechanism for the iodide-promoted reaction is summarized in Figure 1 [43, 56, 57].

The generation of the active nucleophile, $[\text{Co}(\text{CO})_4]^-$, can be considered a water-gas shift reaction [Eq. (4a); cf. Eq. (4b)] in which $[\text{Co}_2(\text{CO})_8]$ is the catalyst and the hydrogen formed is dissociated via the hydridocarbonyl complex.



Subsequently, the methyl iodide formed from hydrogen iodide and methanol undergoes nucleophilic attack by the $[\text{Co}(\text{CO})_4]^-$ anion. Iodide facilitates this reaction because it is a better leaving group than OH^- . The CH_3I reacts with a coordinatively saturated d^{10} complex, which is the preferred electron configuration of cobalt(I). Therefore, the methyl migration to form the acyl cobalt carbonyl complex, $[\text{CH}_3\text{C}(\text{O})\text{Co}(\text{CO})_3]$, is

less favored than the same process for the rhodium(III) species.

Once formed, this acyl intermediate cannot undergo simple reductive elimination of acetyl iodide because iodide is not coordinated to cobalt. Acetyl iodide is formed from the reaction of hydrogen iodide with the acyl complex to regenerate the cobalt carbonyl anion. Rapid hydrolysis of the acetyl iodide forms acetic acid and hydrogen iodide. All of the individual steps involved in the otherwise similar mechanism can be assumed to occur at a lower rate for cobalt than for rhodium and iridium. This explains the higher temperature needed for the BASF process. In addition, higher carbon monoxide partial pressures are required to stabilize the $[\text{Co}(\text{CO})_4]^-$ complex at the higher reactor temperatures.

Byproducts in the BASF process are CH_4 , CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$, CO_2 , $\text{C}_2\text{H}_5\text{COOH}$, alkyl acetates, and 2-ethyl-1-butanol [58–60]. About 3.5 % of the methanol reactant leaves the system as CH_4 , 4.5 % as liquid byproducts, and 2 % is lost as off-gas. Some 10 % of the CO feed is converted to CO_2 by the water gas shift reaction (Eq. 4b).



The *Monsanto process* with rhodium carbonyl catalyst [38255-39-9] and iodide promoter operates under milder conditions than the BASF cobalt-catalyzed process. Methanol and carbon monoxide selectivities of greater than 99 % and 90 %, respectively, are obtained [49]. The system is not as sensitive to hydrogen as the BASF process, and therefore reduction products such as methane and propionic acid are comparatively insignificant.

The chemistry of the rhodium-catalyzed methanol carbonylation reaction has been studied in detail [57]. Kinetic studies show the reaction to be zero-order in carbon monoxide and methanol, and first-order in rhodium and iodide promoter. The carbonylation rate is strongly affected by the reaction media, but the overall kinetics are unaffected by the solvent, which suggests that it does not participate in the transition state of the rate-determining step [61–64]. Methanol carbonylation in polar solvents generally provides a rate enhancement, especially with the addition of protic solvents. An acetic acid/water solvent medium is preferred [65].

Many different rhodium compounds act as effective catalyst precursors for methanol carbonylation at common reaction temperatures of 150 – 200 °C. The iodide promoter is normally methyl iodide, but other forms of iodide, such as hydrogen iodide or iodine, can be used without marked differences in reaction rates.

Spectroscopic investigations have shown that rhodium(III) halides can be reduced in aqueous or alcoholic media to $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ [50]. The reaction rate is independent of the rhodium precursor charged to the reaction provided adequate iodide, generally methyl iodide, and carbon monoxide are available. Under these conditions, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is the predominant rhodium species in the reaction solution. These observations strongly suggest the generation of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ as the active catalyst species [50].

The catalytic cycle shown in Figure 2 is based on kinetic and spectroscopic studies [66–78]. The complex anion $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ reacts in the rate-determining step with methyl iodide by oxidative addition to form the transient methylrhodium (III) intermediate. Methyl migration gives the pentacoordinate acyl intermediate. The acyl intermediate eliminates acetyl iodide and regenerates $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. The acetyl iodide reacts with water to regenerate hydrogen iodide and produce acetic acid. Hydrogen iodide reacts with methanol to form methyl iodide. In this way both the original rhodium complex and methyl iodide promoter are regenerated.

In the 1980s *Celanese* made innovative improvements to the rhodium catalyst system of the Monsanto process with the implementation of the proprietary acetic acid optimization (AO) technology which incorporates catalyst co-promoters. Advantages of AO technology are enhanced carbonylation rates and increased carbon monoxide and methanol efficiencies at lower reaction-water concentrations [52]. These modifications represent the most significant development in rhodium-catalyzed methanol carbonylation since the development of the Monsanto process. The AO technology enabled the Celanese Clear Lake Plant to more than triple unit capacity from 27 000 t/a since start-up in 1978 to 90 000 t/a acetic acid in 1998 with very low capital investment [51, 53].

The increased carbonylation rates at low reaction water concentrations are achieved by catalyst promotion with iodide and acetate

and the rate of methanol carbonylation is increased [38].

Compared to the cobalt-based process, byproducts derived from methanol such as CH_4 , CH_3CHO , and $\text{C}_2\text{H}_5\text{COOH}$ are formed in very small amounts, even in the presence of significant amounts of hydrogen in the carbon monoxide feed gas [82]. This low methanol inefficiency is associated with occurrence of the rate-determining step prior to formation of an organometallic compound, the short lifetime of the methylrhodium complex, and the rapid reductive elimination of the acylrhodium complex to form acetyl iodide, which is rapidly hydrolyzed to acetic acid and hydrogen iodide.

Similar to the rhodium-based carbonylation processes, the reaction chemistry of the BP *iridium-catalyzed methanol carbonylation* is well characterized [50, 56, 57, 78, 85–88]. The iridium-catalyzed reaction proceeds through a series of similar reaction pathways to the rhodium-catalyzed system but involves a different rate-determining step. The proposed rate-determining step is methyl migration to form the iridium acyl complex. This pathway involves the elimination

of iodide and the subsequent addition of carbon monoxide. The direct dependence of the reaction rate on carbon monoxide concentration and the inhibiting effect of low concentrations of iodide are consistent with the rate-determining step [55, 83]. The proposed catalytic scheme for the reaction is given in Figure 3 [55]. Model studies at 25 °C demonstrate that the oxidative addition of methyl iodide to iridium is about 120 – 150 times faster than for rhodium [55, 83]. However, methyl migration on iridium is 10^5 to 10^6 times slower than for rhodium [83]. The main byproducts of the iridium-catalyzed process are also carbon dioxide and hydrogen via the water gas shift reaction (Eq. 4b). The mechanism of this reaction is similar to the rhodium-catalyzed process [57]. The production of CH_4 derived from methanol is higher for iridium than for rhodium. This observation is consistent with the greater stability of the methyliridium(III) complex associated with the hydrogenation of the iridium – carbon bond [83].

Other transition-metal complexes have been investigated as promising catalysts for methanol

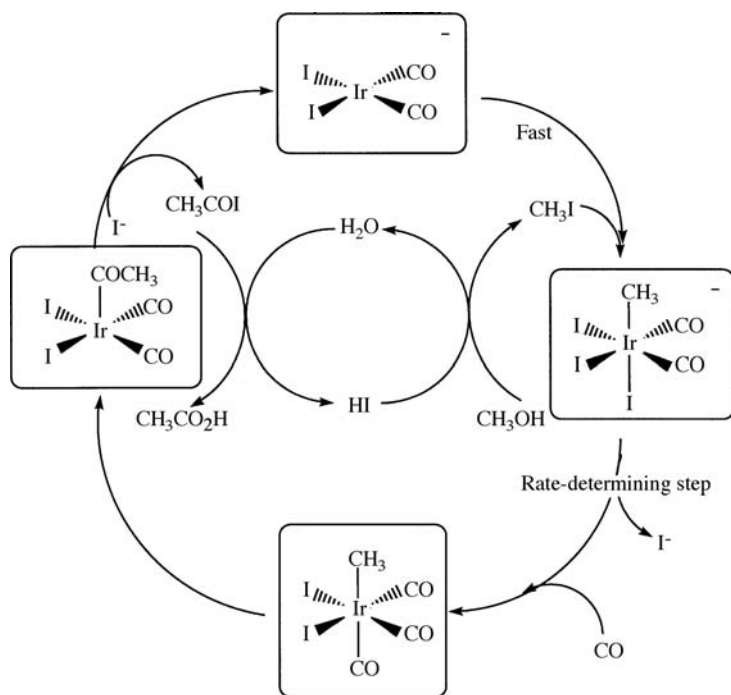


Figure 3. Reaction cycle proposed for the iridium-catalyzed methanol carbonylation reaction (Cativa process)

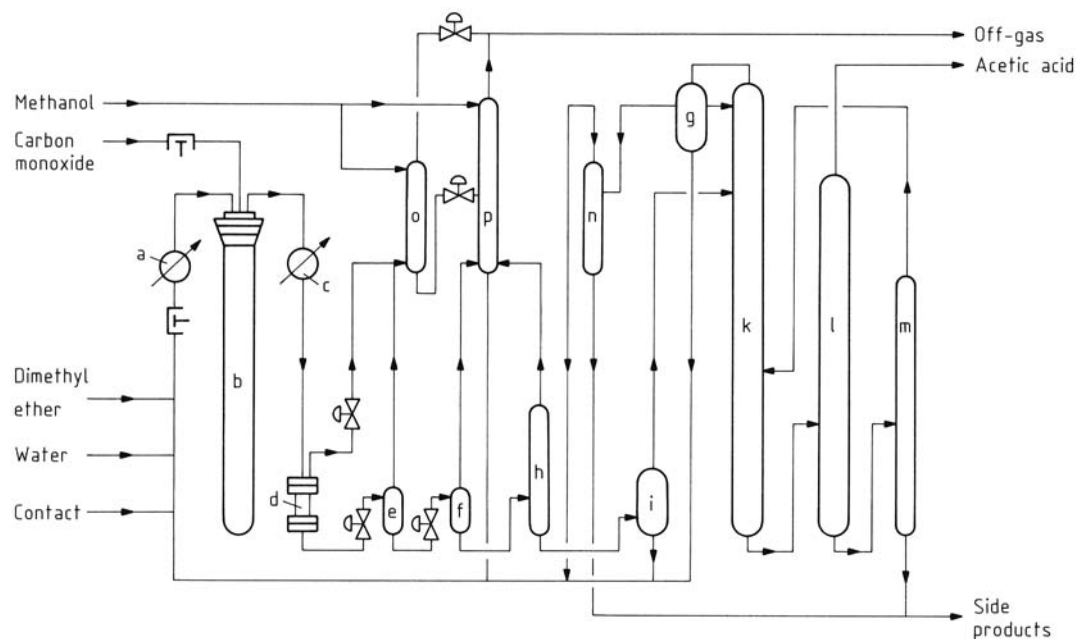


Figure 4. Production of acetic acid (BASF process)

a) Preheater; b) Reactor; c) Cooler; d) High-pressure separator; e) Intermediate pressure separator; f) Expansion chamber; g) Separation chamber; h) Degasser column; i) Catalyst separation column; k) Drying column; l) Pure acid column; m) Residue column; n) Auxiliary column; o) Wash column; p) Scrubbing column

carbonylation, in particular, nickel complexes by Halcon and Rhône-Poulenc [57, 89, 90].

BASF Process [91] (Fig. 4).

Carbon monoxide, methanol (containing up to 60% dimethyl ether), catalyst recycle, catalyst makeup, and methyl iodide recycle (from the wash column) are sent to the high-pressure reactor (b; stainless steel lined with Hastelloy). Part of the relatively low heat of reaction is used to preheat the feed and the rest is ultimately dissipated through the reaction vent. The reaction product is cooled and sent to the high-pressure separator (d). The off-gas goes to the wash column (o) and the liquid is expanded to a pressure of 0.5 – 1.0 MPa in the intermediate-pressure separator (e). The gas released is also sent to the wash column; the liquid from the intermediate-pressure separator is sent to the expansion chamber (f). The gas from the chamber goes to the scrubber (p). The gas from the scrubber and the wash column is discarded as off-gas. Both scrubber and wash column use the methanol feed to recover methyl iodide and other iodine-containing volatile compounds; this

methanolic solution is returned to the reactor. The off-gas composition in vol % is 65 – 75 CO, 15 – 20 CO₂, 3 – 5 CH₄, and the balance CH₃OH.

The raw acid from the expansion chamber contains 45 wt % acetic acid, 35 wt % water, and 20 wt % esters, mainly methyl acetate. The acid is purified in five distillation towers. The first column (h) degasses the crude product; the off-gas is sent to the scrubber column. The catalyst is then separated as a concentrated acetic acid solution by stripping the volatile components in the catalyst separation column (i). The acid is then dried by azeotropic distillation in the drying column (k). The overhead of the drying column contains acetic and formic acids, water, and byproducts that form an azeotrope with water. This overhead is a two-phase system that is separated in the chamber (g). Part of the organic phase, composed mainly of esters, is returned to column (k), where it functions as an azeotroping agent. The remainder of the organic phase is sent to the auxiliary column (n) where heavy ends are separated at the bottom of the column, and light esters from the overhead are recycled to the

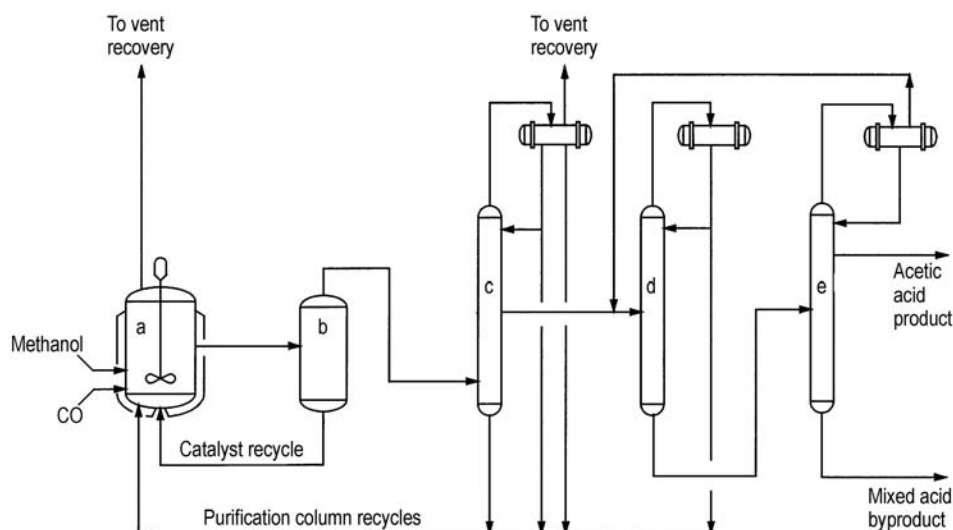


Figure 5. Production of acetic acid (Monsanto process)
 a) Reactor; b) Flasher; c) Light-ends column; d) Dehydration column; e) Heavy-ends column

reactor. The aqueous phase and the catalyst solution are returned to the reactor. The base of the drying column is sent to a finishing column (l), in which pure acetic acid is taken overhead. The bottom stream of the finishing tower is sent to the residue column (m). The overhead of this residue column is sent back to the dehydration column. The bottom of the residue column contains about 50 wt% propionic acid, which can be recovered.

Monsanto Process [38, 83, 92] (Fig. 5).

Carbon monoxide and methanol are introduced continuously into a back-mixed liquid-phase reactor (a) at ca. 150 – 200 °C and 30 – 60 bar [38, 83, 92]. The noncondensable byproducts (CO₂, H₂, and CH₄) are vented from the reactor to control the carbon monoxide partial pressure in the reactor. The off-gas from the reactor and the purification sections of the process are combined and sent to a vent recovery system in which the light ends, including organic iodides such as methyl iodide, are scrubbed from the vent before the noncondensable gases are flared. The light ends from the vent recovery system are recycled to the reactor. The reactor solution is forwarded to the flasher (b) where the catalyst is separated as a residue stream from the crude acetic acid product and recycled to the reactor. The crude acetic acid, which contains methyl iodide, methyl acetate, and water, is taken

overhead in (b) and sent to the light-ends column (c). The light components (methyl iodide, methyl acetate, and water) are recycled to the reactor as a two-phase overhead stream, while wet acetic acid is removed as a side stream from (c) and sent to the dehydration column (d). An aqueous acetic acid overhead stream from (c) is recycled to the reactor and a dry acetic acid product residue stream is forwarded to a heavy ends column (e). As a residue stream in (e), propionic acid, which is the major liquid byproduct of the process is removed with other higher boiling carboxylic acids. Product acetic acid is removed in (e) as a sidestream, and the overhead stream is recycled to the purification section of the process.

Since the Cativa process as demonstrated in the Sterling Plant at Texas City, Texas is a retrofit of the original Monsanto process, the overall general process is presumably the same, possibly with some modifications [54, 93, 94].

4.2. Direct Oxidation of Saturated Hydrocarbons

Liquid-phase oxidation (LPO) of aliphatic hydrocarbons was once practiced worldwide [95]. Due to competition from carbonylation technology, plants have reduced production by LPO significantly. The process changes depending on the availability of raw materials. Raw ma-

Table 5. Butane liquid-phase oxidation processes

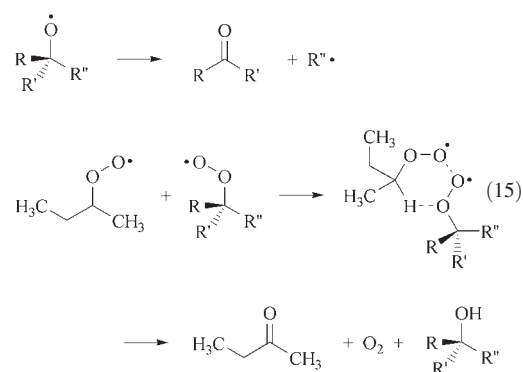
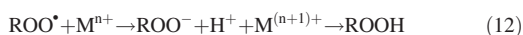
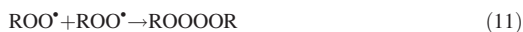
Company	Location	Acetic acid capacity, t/a
Celanese	Pampa, Texas	250 000 [43]
	Edmonton, Alberta, Canada	75 000 [99]
BP	Hull, England	210 000
AKZO Zout Chemie	Europoort, The Netherlands	110 000 [100]

terials include *n*-butane and light naphtha [96]. In the United States and Canada, Celanese employs butane, while BP in the United Kingdom uses light naphtha to produce acetic acid [97]. Capacities of related production are shown in Table 5 [99].

Reaction Mechanism. Oxidation of hydrocarbons follows similar kinetics, both in the gas and liquid phases, especially in slightly polar solvents [98]. However, the mechanism of the reaction is very complicated. The reaction can be considered roughly as a radical chain reaction [99]. For example, the oxidation of butane proceeds through initiation, oxidation, propagation, and decomposition steps [96]. The initiation and propagation probably involve radicals abstracting hydrogen from a secondary carbon atom of butane. Subsequent reaction with oxygen yields hydroperoxides. These intermediates decomposes to produce acetic acid. Catalysts, agitation, and high temperature accelerate the decomposition.

Catalysts are not essential for LPO [100]. However, metal catalysts may influence the distribution of products, induction period, and operating temperature [101, 102].

In a simple mechanism, the first step of oxidation is the abstraction of a secondary hydrogen atom (Eq. 5) to give alkyl radicals. The oxygen in the solvent rapidly converts these radicals to *sec*-butylperoxy radicals [103] (Eq. 6). In other interpretations, oxygen is believed to directly react with one or two alkane molecules to form radicals (Eqs. 7 and 8) [104–106]. Initiation, especially with catalysts, affects the induction period significantly [107].



In general, peroxy radicals do not abstract hydrogen efficiently from other molecules, so the reaction medium contains an abundance of these radicals. Each radical abstracts hydrogen from an alkane to form a hydroperoxide and an alkyl radical (Eq. 9). Alkyl radicals propagate the chain (Eq. 6).

The hydroperoxide decomposes to give an alkoxy radical by thermolysis. The radical undergoes a bimolecular reaction to terminate the formation of radicals (Eq. 11). In the steady state, the termination of radicals is balanced by their production. This mechanism is too simple to explain the reaction in detail. In real systems, thermolysis may not be the only course of decomposition [108].

Alternatively, hydroperoxides may come from the complexation of metal catalysts with peroxy radicals (Eq. 12). Hydroperoxide radicals generate new radicals (Eqs. 10, 13). Therefore, the catalyst is important in maintaining a constant flux of radicals. However, in certain cases, catalysts may actually inhibit the decomposition [109].

Manganese and cobalt are common catalysts for LPO. These metals accelerate the decomposition of hydroperoxide. There is evidence that manganese may enhance the oxidation of ketone intermediates through a mechanism involving enols [110].

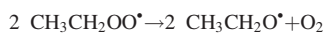
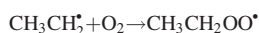
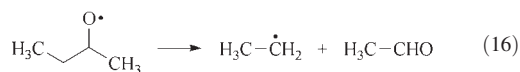
The peroxy radicals terminate by forming tetroxides (Eq. 11), which decompose to yield alkoxy radicals and oxygen (Eq. 14).

If the tetroxide has an α -hydrogen atom, the decomposition may follow a Russel mechanism [111]. The products are oxygen, a ketone, and an alcohol (Eq. 15). However, the mechanism is controversial. Recent reports both support [112] and challenge the mechanism [113].

Besides hydrogen abstraction, alkoxy radicals can participate in β -scission (Eq. 16). Products vary depending on the structure of the radicals. Primary, secondary, and tertiary alkoxy radicals yield alcohols, aldehydes, and ketones, respectively.

The mechanism of butane oxidation is complex. However, with detailed understanding of product distribution and rates, a mathematical model was developed [103].

About 25 % of the carbon of consumed butane appears as ethanol in the initial step as the first isolable non-peroxidic intermediate. The reaction probably involves decomposition of *sec*-butoxy radicals to form acetaldehyde and an ethyl radical (Eqs. 16, 17). Another source of acetaldehyde is the oxidation of ethanol. Acetaldehyde then reacts rapidly to produce acetic acid. Therefore, acetaldehyde is a major intermediate in butane LPO.



Besides acetaldehyde, 2-butanone or methyl ethyl ketone is another major byproduct. The ketone is the result of the termination of *sec*-butylperoxy radical by the Russel mechanism (Eq. 15).

Other impurities include propionic acid and butyric acid. *sec*-Butoxy radicals undergo β -scission to yield propionaldehyde. Oxidation of the aldehyde gives propionic acid. Butyric acid is derived from *n*-butyl radicals.

Higher paraffins are oxidized by similar mechanisms to that of butane. However, the products include shorter chain methyl ketones and difunctional intermediates. These are the results of intramolecular hydrogen abstraction. European countries usually produce acetic acid from naphtha since naphtha is cheap and available. However, the naphtha-based processes yield large amounts of impurities that increase the cost of purification.

Industrial Operation [6, 114–116] (Fig. 6).

Air or oxygen-enriched air can be used as the oxidant. Multivalent metal ions, such as Mn, Co, Ni, and Cr, are used as catalysts. Some processes,

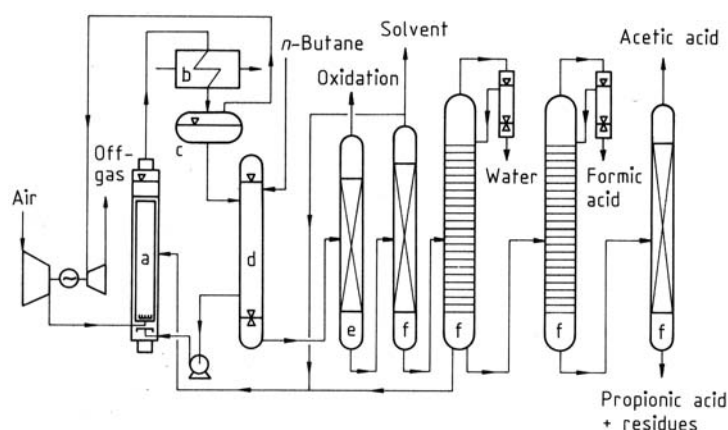


Figure 6. Oxidation of *n*-butane in the liquid phase (Chemische Werke Hüls process)
a) Reactor; b) Air cooler; c) Collector; d) Separation vessel; e) Pressure column; f) Distillation column

however, are noncatalytic. Reaction conditions are 150 – 200 °C for a range of reaction pressures that include 5.6 MPa. The reaction pressure for naphtha oxidation is lower. The reaction solvent consists of acetic acid, varying amounts of intermediates, water, and dissolved hydrocarbons. Control of the water concentration below some maximum level appears to be critical.

The reaction section (a – d) of a liquid-phase oxidation unit consists of a staged tubular reactor or column (a) and one or more phase separation vessels (b – d) for separating the gas and two liquid phases from the reactor. The hydrocarbon vapor exiting the reactor (a) can be recovered for recycling. Normally the reactor vapor is expanded through a turbine (b) to recover duty to compress air for use in the reactor. The consequent reduction in temperature condenses the hydrocarbon. The top organic layer from the phase separator (d) is rich in hydrocarbons and is recycled to the reactor. The bottom, aqueous layer, is distilled to recover the hydrocarbon for recycle.

The residual, hydrocarbon-free product consists of volatile, neutral oxygenated derivatives (aldehydes, ketones, esters, and alcohols), water, volatile monocarboxylic acids (formic, acetic, propionic, and butyric from butane), and nonvolatile materials (difunctional acids, γ -butyrolactone, condensation products, catalyst residues, etc).

The volatile neutral substances can be recovered as mixtures or individually. They are used for derivatives, sold, or recycled to the reactor. Most of these components generate acetic acid on further oxidation.

The separation of water and formic acid from acetic acid involves several distillations (f). Water removal is the most difficult and costly step of the purification process. It is accomplished by azeotropic distillation with entrainment agents, such as ethers, or by extractive methods.

Formic acid is separated from the resulting anhydrous acetic acid usually by fractionation with an azeotroping agent. The remaining higher boiling acids are separated from acetic acid as a residue stream by fractionation.

In some cases, hydrocarbons such as heptane and isooctane can be added to the reactor to improve separation. These chemicals form a high-boiling azeotrope with formic acid.

In the case of naphtha oxidation, diacids such as succinic acids are isolated for sale [117]. The

nonvolatile residue can be burned to recover energy.

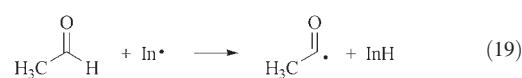
4.3. Acetaldehyde Process

Oxidation of acetaldehyde represents a major process for making acetic acid [6, 8] (Eq. 18).

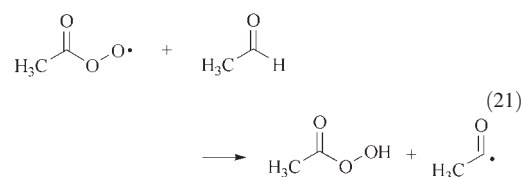
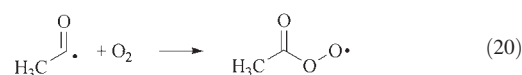


Although oxidation reactions are rather complex, a simplified view is presented here. The oxidation of acetaldehyde to acetic acid proceeds through a free-radical chain which produces peracetic acid as an intermediate.

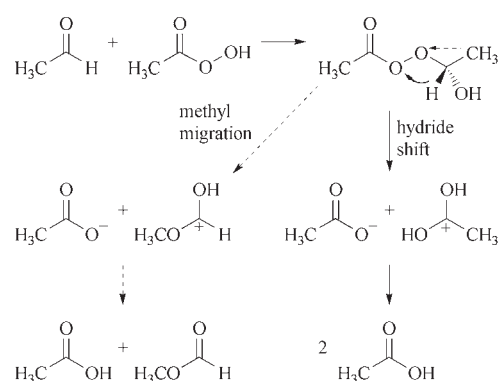
Iniation:



Propagation:

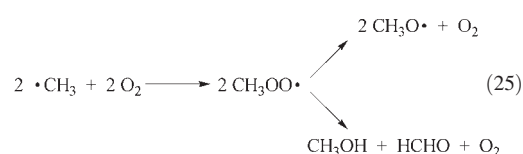
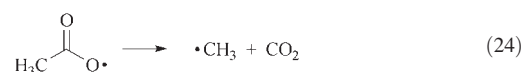
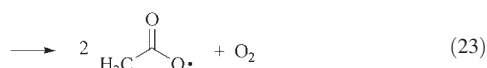
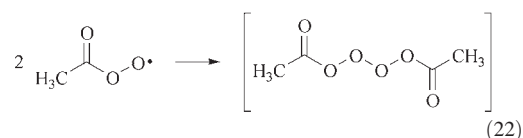


Peracetic acid reacts with acetaldehyde to generate acetaldehyde monoperoacetate [7416-48-0]. The acetaldehyde monoperoacetate decomposes efficiently to acetic acid by a hydride shift in a Baeyer – Villiger reaction. The methyl migration leads to the byproduct methyl formate [118]:



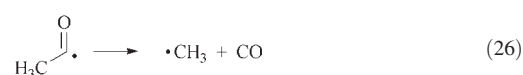
The alkyl migration becomes more pronounced with higher aldehydes, particularly aldehydes having a branch at the α -position.

Chain termination occurs primarily through bimolecular reactions of acetylperoxy radicals via an intermediate tetroxide (Eq. 22). [119].



Equations (23) – (25) are the source of most of the carbon dioxide, methanol, formaldehyde, and formic acid byproducts. Uncatalyzed oxidation is efficient so long as the conversion of acetaldehyde is low and there is a significant concentration of aldehyde in the solvent. This keeps the steady state concentration of acetylperoxy radicals low and favors the Baeyer – Villiger reaction over the reactions (23) – (25). Special precautions must be taken in the uncatalyzed reaction to prevent the concentration of acetaldehyde monoperoxide from reaching explosive levels [6].

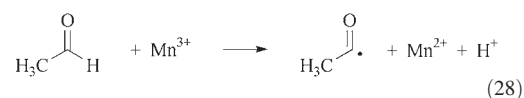
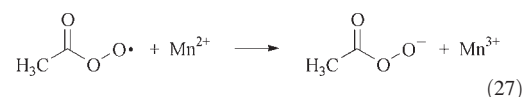
At low oxygen concentrations another free-radical decomposition reaction becomes important (Eq. 26).



The rate of decarbonylation increases with increasing temperature. Decarbonylation becomes significant when insufficient oxygen is present to scavenge the acetyl radicals.

Catalysts can play several important roles in aldehyde oxidations [120]. Catalysts decompose peroxides and so minimize the explosion hazard (Eq. 27). In addition, manganese also reduces acetylperoxy radicals [121] directly to peroxy

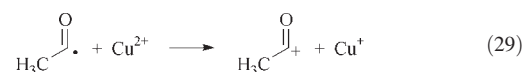
anions [122]:



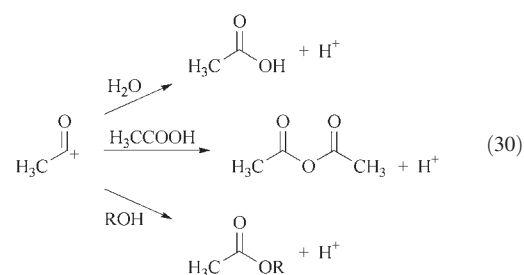
Reaction with Mn^{2+} assists in suppressing the concentration of acetylperoxy radicals. The Mn^{3+} formed can generate the acyl radical for the propagation step (Eq. 28), but does not contribute to inefficiency-generating reactions.

Manganese also greatly increases the rate of reaction of peracetic acid and acetaldehyde to produce acetic acid [123]. The reaction in the presence of manganese is first-order with respect to peracid, aldehyde, and manganese. In addition, the decomposition replenishes the supply of radicals. This is important since the oxidation requires a constant flux of radicals. Manganese ions increase both the rate and efficiency of oxidation.

Copper can interact synergistically with a manganese catalyst [124]. Manganese has some negative aspects associated with the fact that it greatly increases the reaction rate [125]. The increased reaction rate leads to oxygen starvation and an increasing steady state concentration of radicals. Both contribute to byproduct formation by decarbonylation and decarboxylation. However, Cu^{2+} can oxidize acetyl radicals very rapidly (Eq. 29) [126].



The acetylium ion can react as shown in Equation (30).



Peroxide or Mn^{3+} can reoxidize the Cu^+ . Copper diverts a fraction of the reaction through

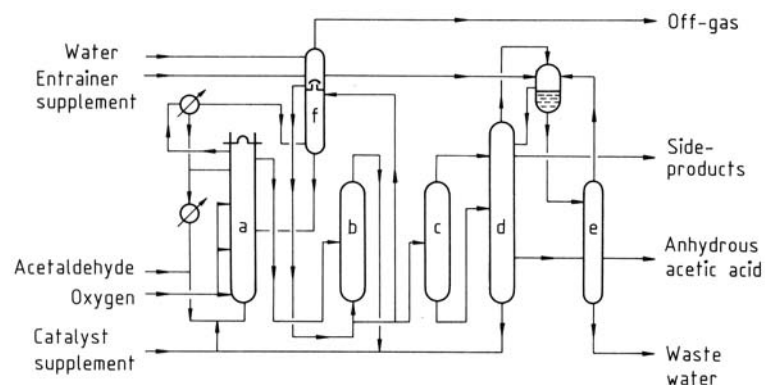


Figure 7. Oxidation of acetaldehyde to acetic acid
 a) Reactor; b) Acetaldehyde column; c) Methyl acetate column; d) Finishing column; e) Column for recovering entrainer; f) Off-gas scrubber column

a nonradical pathway and consequently provides a termination step that does not result in inefficiency.

Another effective catalyst is cobalt. At low concentration, this catalyst shortens the induction period [126]. The cobalt catalyst is regenerated by decomposing peracetic acid. In kinetic studies [127], CH_3CO_3 was the main free radical in the liquid phase. Other catalysts, for example phosphomolybdic acids [128], also catalyze acetaldehyde oxidation.

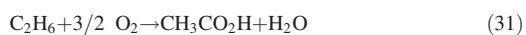
Additional byproducts from acetaldehyde oxidation include ethylidene diacetate, crotonic acid, and succinic acid.

Industrial Operation. A typical acetaldehyde oxidation unit is depicted in Figure 7. The reactor (a) is sparged with air or oxygen-enriched air. Temperatures are typically 60 – 80 °C with pressures of 0.3 – 1.0 MPa. The reaction mixture is circulated rapidly through an external heat exchanger to remove the heat of reaction. The vent gas is cooled and then scrubbed with recirculated crude product (which goes to the reactor) and finally with water (which goes to the aldehyde recovery column). The reactor product is fed to the aldehyde recovery column (b), from which the aldehyde is recycled, and then to a low-boilers column (c) in which methyl acetate is removed. The next column is the acetic acid finishing column (d), where water is removed overhead by azeotropic distillation and finished product comes off as a vapor sidestream. Yields are generally in excess of 90 % and purity is greater than 99 %.

4.4. Other Processes

Acetic Acid from Ethylene. Efforts to convert ethylene directly to acetic acid without going through an acetaldehyde isolation step have been of interest. Although the price of ethylene generally makes this process unattractive, some developments are noteworthy. Effective oxidation of ethylene to acetic acid has been demonstrated with metal oxides such as vanadium pentoxide. SEONE et al. [129] demonstrated that the presence of palladium enhances ethylene oxidation to acetic acid as temperatures as low as 230 °C. Showa Denko combined palladium with heteropolyacids and patented a catalyst for producing acetic acid from ethylene and oxygen. The catalyst contains palladium, a heteropolyacid, such as silicotungstic acid, and potassium tellurite or potassium selenite. The process is operated at 150 °C and 0.7 MPa. Although water is not consumed in the reaction, the presence of water enhances the selectivity to acetic acid and is recommended.

Acetic Acid from Ethane. Several groups have investigated catalysts for the conversion of ethane to acetic acid (Eq. 31).



Union Carbide [130] developed the Ethoxene process for the production of ethylene from ethane and oxygen. The earliest catalysts consisted of molybdenum, vanadium, and niobium oxides and were very selective for ethylene at

temperatures below 300 °C. Unfortunately, ethane conversions were low (about 10 %) due to inhibition by the product. Further development [131] focused on the coproduction of ethylene and acetic acid with a catalyst comprised of molybdenum, vanadium, niobium, calcium, and antimony. The addition of water enhances acetic acid formation. A later patent [132] discloses that the addition of water and an ethylene hydration catalyst improves selectivity to acetic acid.

Rhône-Poulenc [133, 134] has patented a process to make acetic acid from ethane with a vanadium oxide or vanadyl pyrophosphate supported on titanium dioxide. Tessier et al. [135] found that acetic acid production was favored over ethylene and carbon oxides at temperatures below 300 °C. Roy et al. [136] demonstrated that the addition of molybdenum enhanced acetic acid selectivity. Desorption of acetic acid from the catalyst surface was speculated to be the rate-determining step of the reaction.

BP Chemicals [137, 138] claims that the addition of rhenium to mixed metal oxide catalysts enhances selectivity to acetic acid from the oxidation of ethane and/or ethylene. Again, water is used to enhance selectivity to acetic acid. Standard Oil [139] claims good selectivity to acetic acid with a vanadyl pyrophosphate catalyst containing a transition metal. Hoechst [140] claims a catalyst containing molybdenum and palladium as effective for the production of acetic acid from ethane. An acetic acid selectivity of 84 % was attained at 250 °C and 7 bar with a 14-s residence time.

Although ethane is an inexpensive raw material and high selectivities to acetic acid have been achieved, it is unlikely that ethane oxidation will compete with methanol carbonylation in the near future. The oxygen concentration must be limited for safety reasons and therefore ethane conversion is limited per pass in the reactor. Although staged addition of oxygen is possible, product inhibition remains a problem and limits ethane conversion. Since the addition of water is needed to improve selectivity to acetic acid, water must be removed from the acetic acid, usually by extractive distillation.

Acetic Acid from Microorganisms Since about 10 000 B.C., aqueous solutions of acetic

acid have been prepared from spoiled wine [141, 142]. Ethanol and sugar were the primary feedstocks for microorganism production of acetic acid, although biomass has been proposed [143]. The concentration of acetic acid in solution is limited by the ability of bacteria to thrive in low-pH solutions. Consequently, researchers have focused on improving acetic acid productivity and lowering the pH of the bacterial culture. Mutant strains of *Clostridium thermoaceticum* [144] have been developed to produce acetic acid in solutions below pH 5. Improvement of acetic acid productivity of an *Acetobacter aceti* strain was achieved by amplification of the aldehyde dehydrogenase gene with a multicopy vector [145]. Bacterial production is gaining interest since it is an environmentally friendly process. Nevertheless, cost-effective acetic acid concentration and purification remain a challenge.

4.5. Concentration and Purification

In most commercial processes acetic acid is purified from an aqueous acetic acid solution by straight distillation methods that are economically viable provided the acetic acid is in high concentrations when initially isolated from the reaction system of the process. Other acetic acid purification techniques can be used, in particular, for dilute acetic acid such as byproduct streams of important industrial processes, e.g., cellulose acetate production (\rightarrow Cellulose Esters). Azeotropic distillation, solvent extraction, and extractive distillation can recover acetic acid from these aqueous streams. Direct distillation requires a significant number of plates and a high reflux ratio in the columns. In extractive distillation, the vapor streams of acetic acid and water are scrubbed with a high-boiling solvent that preferentially dissolves one of the components.

Azeotropic Distillation. In azeotropic distillation, a compound that decreases the boiling point of water is used. If the azeotropic agent is immiscible with water, it can be separated easily from water and recycled. Esters, ethers, benzene, and chlorinated hydrocarbons have been proposed as azeotropic agents [146].

Solvent Extraction. Acetic acid is removed from aqueous solutions (0.5 – 5 wt % acetic acid) by solvent extraction. The aqueous solution is contacted with an organic solvent, often containing an organic base, and then acetic acid is stripped from the base in a distillation process and separated from the cosolvent, usually an alkane, by phase separation. Consequently, it is important for the organic solvent to have a high affinity for acetic acid relative to water. Primary amines are generally not suitable extraction additives due to their water solubility. Secondary amines have high extraction coefficients [147] but can form amides during the acid recovery process. Tertiary amines such as trioctylamine [148] have extraction coefficients which are strongly dependent on amine concentration and the cosolvent used. EYAL and CANARI [149] discuss how anion exchange, ion-pair formation, hydrogen-bond formation, and solvation all play important roles in amine-based extraction of acetic acid. In addition to amines, dibutyl phosphonate [150] and trioctyl phosphine oxide [151] have high extraction coefficients relative to alcohols, ethers, or esters.

The selection of a water-removal method depends on economics. Extraction is generally preferred at low concentrations of acetic acid.

4.6. Construction Materials [152, 153]

Little is known about construction materials for equipment in acetic acid processes. The information on materials is usually considered a trade secret. Liquid streams containing acetic acid corrode metals. The corrosion increases with increasing concentrations of acetic acid, halides, and formic acid. High temperatures ($> 200\text{ }^{\circ}\text{C}$) also increase the corrosion rate. AISI 316 stainless steel [12597-68-1] is used for processes without reducing agents and halides. In the presence of reducing agents, AISI 321 stainless steel is necessary. Hastelloy B or C or other materials are required if halides are present. Aluminum [7429-90-5] and AISI 304 stainless steel are used in storage tanks, pumps, and piping at room temperature and high acid concentrations. AISI 316 stainless steel contains 16 – 18 wt % Cr, 10 – 14 wt % Ni and 2 – 3 wt % Mo. AISI 321 stainless steel has 17 – 19 wt % Cr, 9 – 12 wt % Ni and > 0.4 wt % Ti. AISI 304 stain-

less steel is comprised of 18 – 20 wt % Cr and 8 – 10.5 wt % Ni.

5. Wastewater and Off-Gas Problems [154]

Waste streams from acetic acid process usually contain residual acetic and formic acids. These acids must be recycled, diluted, or treated chemically and then degraded biologically. European countries require neutralization or biological degradation of these waste streams [6, 8].

Acetic acid is corrosive and can damage human skin and internal organs. Acetic acid should be handled with care to avoid breathing vapors. If a spill occurs, neutralize soil and wash with soda ash or lime. The Clean Water Act (USA) and Superfund (USA) dictate that a reportable quality (RQ) of 2270 kg (5000 lb) [155].

In Germany [156], no more than 3 kg/h may be emitted in vent gases, with a maximum of 150 mg/m^3 . The vent gas is scrubbed or chilled to eliminate the acids.

Under the same German regulations, the maximum emissions for methyl acetate, ethyl acetate, butyl acetate, and phenyl acetate are 300 mg/m^3 . The off-gas is limited to 6 kg/h [8]. The recommended methods of removal of the acetic acid are thermal condensation, washing with nonvolatile organic solvent, physical absorption or burning.

In the United States, the United States Clean Air Act governs the amount of emissions. Each state also sets individual emission limits. The limits range from 0.25 mg/m^3 to 0.37 mg/m^3 (North Dakota), to 0.4 mg/m^3 (Virginia) to 0.5 mg/m^3 (Connecticut and South Dakota) to 0.595 mg/m^3 (North Carolina) [154].

6. Quality Specifications

There is essentially one commercial grade of acetic acid sold in the United States. Elsewhere, three or more grades are available differing as to specifications for heavy metals, chloride, sulfate, arenic, and iron [157]. Also, depending on specific end uses, additional product criteria must be considered. For example, in the manufacture of vinyl acetate, halides are important since they are a catalyst poison in vinyl acetate processes. One

Table 6. Sales specifications for glacial acetic acid [76]

Sales specifications	Limits	
Acetic acid, wt %	min.	99.85
Distillation range (including 118.1), °C	max.	1.0
Freezing point, °C	min.	16.35
Color, Pt – Co units	max.	10
Water content, wt %	max.	0.15
Reducing substances, as formic acid, wt %	max.	0.05
Aldehydes, as acetaldehyde, wt %	max.	0.05
Iron, ppm	max.	1
Heavy metals, as Pb, ppm	max.	0.05
Chlorides, ppm	max.	1
Sulfates, ppm	max.	1
Sulfurous acid, ppm	max.	1
Permanganate time	min.	2 h

of the most critical specifications for all end uses of acetic acid is “permanganate time.” The test for “permanganate time” is a semi-quantitative wet method for the measurement of oxidizable impurities. One manufacturer’s sales specification is given Table 6 [76].

7. Analysis

Gas chromatography is the usual technique for determining the acetic acid content of a volatile mixture. Packed columns can be used, but capillary columns are preferred. Carbowax 20M, terephthalic acid terminated [41479-14-5], is the preferred substrate.

8. Storage, Transportation, and Customs Regulations [8, 152, 159]

DOT regulations regard glacial acetic acid (99.7 %) as a hazard. The acid belongs to UN/DOT Hazard Class 8 and Shipping Group II [160]. Acetic acid should be stored in a cool, dry place away from contact with oxidizing materials. Containers should be kept closed and labeled as “Corrosive”. Precautionary labels such as “Flammable” are recommended. Even when emptied, the containers may still retain acid residue. Wash the container with water. The emptied container should still have a warning label.

The acid can be stored and transported in containers lined with stainless steel, glass, or polyethylene. Another material for containers is

aluminum. Aluminum forms a protective coating of aluminum oxide or aluminum acetate when exposed to acetic acid. The coating prevents further corrosion. Caution is warranted to prevent water and mercury contamination. Water and small amounts of mercury accelerate the corrosion. Maintaining a high acid concentration and not using a mercury thermometer help to prevent catastrophic corrosion.

The limits for shipping concentrated acetic acid in passenger aircraft or railcar is 1 L, and 30 L in cargo aircraft. Acetic acid has a low melting point of 16 °C. Transporting the acid in cold weather requires the vessels to be heated. Storage containers, tank trucks, and pipes for concentrated acid should be equipped with heated coils. Storage vents also need to be heat traced to prevent the acid from crystallizing.

German Legal Requirement for Food-stuffs. Commercial vinegar exceeding 11 wt % acetic acid may be sold in closed containers. The material of the containers should be resistant to acetic acid. The container must be clearly marked with a label warning as “Handle with Care.”, “Do Not Swallow Undiluted.” Solutions containing more than 25 wt % acetic acid are not available to the public. Commercial dealers are allowed to handle the acid.

German Customs Requirements (Vinegar Law) [5]. The Vinegar Law, Paragraph 1, dictates that the transfer of synthetic vinegar in retail markets is taxable. The tax is known as the Vinegar Tax. Both imported and local products are subjected to the tax. With changing of vinegar price, the tax is adjusted.

Tax exempt status is granted for acetic acid used in commercial purposes. Another case for tax exempt status also deals with commercial uses where the acid is consumable by humans.

9. Uses

Acetic acid has a broad spectrum of applications. An outline of these is given in Figure 8 [1, 48]. Greater than 65 % of the acetic acid produced worldwide goes into polymers derived from vinyl acetate (→ Vinyl Esters), or cellulose (→ Cellulose Esters). Most of the poly(vinyl acetate) is used in paints and coatings or

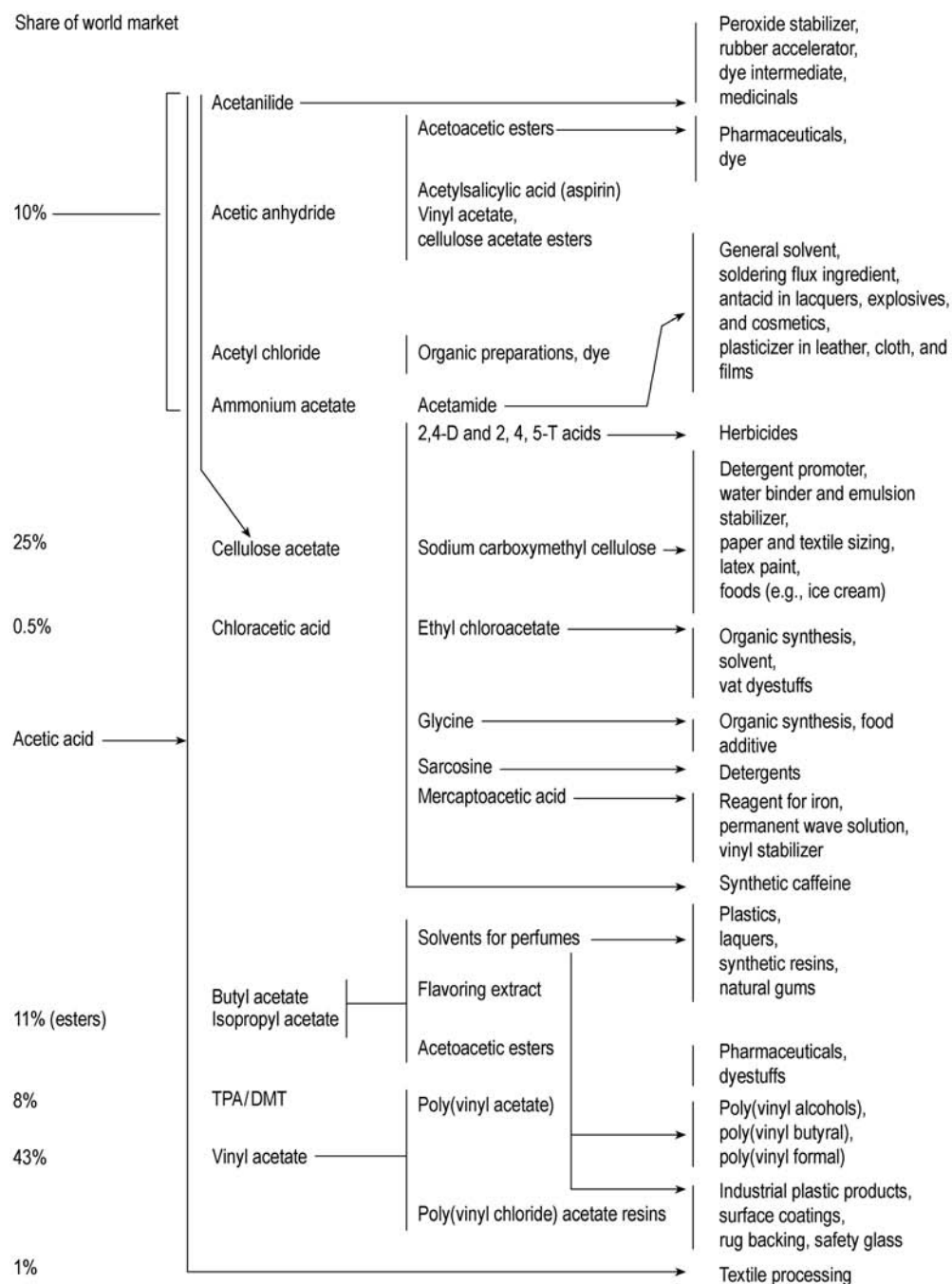


Figure 8. Uses of acetic acid

for making poly(vinyl alcohol) and plastics. Cellulose acetate is used to produce acetate fibers. Acetic acid and acetate esters are used extensively as solvents.

10. Derivatives

This section contains information about acetic acid derivatives that are not discussed in detail elsewhere in this encyclopedia (→ Acetic Anhydride, → Cellulose Esters, → Chloroacetic Acids, → Esters, Organic, → Vinyl Esters).

10.1. Salts

10.1.1. Aluminum Acetate

Three aluminum acetates are known, two basic and one neutral: $\text{Al}(\text{OH})_2\text{CO}_2\text{CH}_3$ [24261-30-1], $\text{Al}(\text{OH})(\text{CO}_2\text{CH}_3)_2$ [142-03-0], and $\text{Al}(\text{CO}_2\text{CH}_3)_3$ [139-12-8].

Properties. $\text{Al}(\text{CO}_2\text{CH}_3)_3$, M_r 204.1, is a white, water-soluble powder that decomposes at about 130 °C to give acetic anhydride along with basic aluminum acetates [161].

Production. Neutral aluminum acetate is made from aluminum metal and glacial acetic acid that contains 0.1 – 1 % acetic anhydride, which scavenges any water present [162]. The anhydrous triacetate cannot be made from aqueous solutions. The basic acetates can be prepared from $\text{Al}(\text{OH})_3$ and aqueous acetic acid solutions [163].

Uses. Aluminum acetate is used as a dye mordant in the dyeing of fabrics.

10.1.2. Ammonium Acetate

Properties. Ammonium acetate [631-61-8]. $\text{CH}_3\text{CO}_2\text{NH}_4$, M_r 77.08, mp 114 °C, forms colorless, hygroscopic needles. The solubilities of this salt in 100 g of water or methyl alcohol are, respectively, 148 g (4 °C) and 7.9 g (15 °C).

Production. Ammonium acetate is manufactured by neutralizing acetic acid with ammonium

carbonate or by passing ammonia gas into glacial acetic acid [114]. Acidic ammonium acetate, $\text{CH}_3\text{CO}_2\text{NH}_4 \cdot \text{CH}_3\text{CO}_2\text{H}$ [25007-86-7], is manufactured by dissolving the neutral salt in acetic acid.

Uses. Ammonium acetate is used in the manufacture of acetamide and as a diuretic and diaphoretic in medical applications. The wool industry also uses this salt as a dye mordant.

10.1.3. Alkali Metal Salts

Properties. All of the alkali metals (Li, Na, K, Rb, Cs) form acetates. The aqueous solubilities of these salts increase with increasing atomic mass of the alkali metal [164]. The potassium salt [127-08-2], M_r 98.14, mp 292 °C, and sodium salt [127-09-3], M_r 82.04, mp 324 °C, are the most common. The former crystallizes from water as white columns. The latter can be purified by crystallization from acetic acid. Several acetic acid solvates of the alkali metal salts are known [163].

Production. Potassium and sodium acetates normally are manufactured from glacial acetic acid and the corresponding hydroxides. The salts also can be prepared from acetic acid on treatment with the metal, the metal carbonate, or the metal hydride [163].

Uses. Potassium acetate is used to purify penicillin. It is also used as a diuretic and as a catalyst to make polyurethane. The sodium salt is used frequently in water as a mild alkali.

10.2. Esters (→ Esters, Organic)

[166–169]

Properties. Physical properties of acetate esters are listed in Table 7 [168].

Production. The reaction of an alcohol and an organic acid produces an ester in the presence of an acid catalyst [166]. The reaction, esterification, is the most common process for manufacturing acetate esters (Eq. 32).

Table 7. Physical properties of acetate esters

Ester	CAS no.	M_r	n_D^{20}	n_{20}^{20}	$bp, ^\circ C$	$fp, ^\circ C$	Flash pt., $^\circ C$
Methyl acetate	[141-78-6]	74.1	1.36	0.93	57.0	-98.1	-10
Ethyl acetate	[108-05-4]	88.1	1.37	0.902	77.1	-83.6	-4
Propyl acetate	[109-60-4]	102.13	1.38	0.887	101.6	-92.5	13
Isopropyl acetate	[108-21-4]	102.13	1.38	0.872	90.1	-73.4	2
Butyl acetate	[123-86-4]	116.16	1.39	0.882	126.0	-73.5	22
Isobutyl acetate	[110-19-0]	116.16	1.39	0.871	117.2	-98.6	18
sec-Butyl acetate	[105-46-4]	116.16	1.39	0.876	112.0		31
tert-Butyl acetate	[540-88-5]	116.16	1.39	0.867	97.0		
n-Pentyl acetate	[628-63-7]	130.18	1.40	0.876	149.2	-70.8	
2-Ethylhexyl acetate	[103-09-3]	172.26	1.42	0.873	199.3	-93.0	71



Other industrial processes include the reaction of acetic anhydride with alcohols and the Tishchenko reaction. Other methods for synthesizing acetate esters are the addition of acetic acid to olefins, carbonylation of acetic acid or anhydride, and reductive methods involving carboxylic acids or anhydride.

Commercial processes for esterification are usually continuous and are performed in the liquid phase. The reaction requires strong acids such as sulfuric acid or organic sulfonic acids. Another type of catalyst is ion-exchange resins. In contrast, gas-phase technology is available with sulfonated polymer [170] or supported phosphoric acid as catalyst [171].

Esterification involves an equilibrium between reactants and product (Eq. 33). Adding excess reactants or removal of water drive the equilibrium to favor the formation of ester. Azeotroping agents eliminate water and force the reaction to completion. Common agents are cyclohexane, benzene, and toluene.

$$K_{eq} = \frac{[CH_3COOR][H_2O]}{[CH_3COOH][ROH]} \quad (33)$$

Esterification with acetic anhydride offers an alternative route for making acetates. Due to its high reactivity, acetic anhydride readily forms esters with alcohols. The reaction is irreversible. The esterification goes to completion without eliminating products or water.

Additions of acetic acid to olefins present an alternative way to make acetates, especially for branched esters. Synthesis of these hindered esters by esterification is not efficient. The equilibrium does not favor the desirable products. Rhône-Poulenc uses this method to prepare iso-

propyl acetate from acetic acid and propylene [172]. Catalysts can be strong protic or Lewis acids, like sulfuric acid or $BF_3 \cdot OEt_2$ [173]. Ethyl acetate can also be produced directly from acetaldehyde.

Adding hydrogen and carbon monoxide to acetic acid or acetic anhydride can produce acetates. Alternatively, hydrogenation of acetic acid yields ethanol and ethyl acetate. Many studies relate to supported heterogeneous catalysts with molybdenum and group VIII metals (Pd, Rh, or Ru). Additionally, homogeneous catalysis with ruthenium can result in high selectivity [172].

Commercial processes also include the reaction of aldehydes to make esters. The Tischenko reaction uses alkoxide catalysts. Typical catalysts are aluminum alkoxide, boric acid and magnesium or calcium aluminum alkoxides [173].

Uses. Applications of acetates depend on their physical properties such as boiling point and evaporation rate. Therefore, uses of acetates cover many products such as coatings, solvents for plastics, lacquers, resins, and gums.

10.2.1. Methyl Acetate

Properties. Methyl acetate is colorless and has a pleasant odor. Methyl acetate forms azeotropes with water (3.5 wt% H_2O , bp 56.5 $^\circ C$) and methanol (19 wt% $MeOH$, bp 54.0 $^\circ C$). Other properties are listed in Table 7.

Production. Most commercially available methyl acetate is a byproduct in the manufacture of acetic acid. Another method is the esterifica-

tion of methanol and acetic acid with sulfuric acid as catalyst. The product ester is removed as the methanol/methyl acetate azeotrope.

Uses. Methyl acetate has the lowest boiling point (55.8 – 58.2 °C) of all organic acetates. It evaporates about five times faster than butyl acetate [166]. Therefore, methyl acetate finds uses where rapid evaporation is necessary. It is employed as a process solvent for preparing cellulose nitrates. Transesterification to make esters uses methyl acetate as a reagent. In addition, the production of acetic anhydride requires the acetate.

10.2.2. Ethyl Acetate

Properties. Ethyl acetate has a pleasant odor. It forms azeotropes with water (8.2 wt % H₂O, *bp* 70.4 °C), ethanol (30.8 wt % EtOH, *bp* 71.8 °C), and methanol (44 wt % MeOH, *bp* 60.2 °C). With water and ethanol, the ester forms a ternary azeotrope (7.8 wt % H₂O, 9.0 wt % EtOH, *bp* 70.3 °C). Other properties are listed in Table 7.

Production. Ethyl acetate is made from ethanol [64-17-5] and acetic acid in batch or continuous processes. A major step in the continuous process is the removal of the ester. The distillation process separates the ester by taking advantage of the alcohol – ester – water azeotrope. After decanting and purification, the final yield of the ester can reach as high as 95 %.

Another means of making ethyl acetate is the Tischenko reaction. Two moles of acetaldehyde can undergo bimolecular reaction to yield ethyl acetate with a metal alkoxide catalyst at low temperature (Eq. 34). A popular catalyst is aluminum alkoxide.

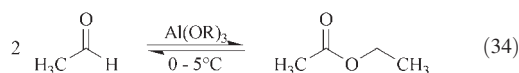


Table 9. Ternary azeotropes with the butyl acetates

Component A	Component B	Component C	<i>bp</i> , °C	wt % B	wt % C
<i>n</i> -Butyl acetate	Water	<i>n</i> -Butanol	89.4	37.3	37.3
<i>sec</i> -Butyl acetate	Water	2-Butanol	86.0	23.0	45.0
Isobutyl acetate	Water	Isobutyl alcohol	86.8	30.4	23.1

Table 8. Binary azeotropes with the butyl acetates

Component A	Component B	<i>bp</i> , °C	wt % B
<i>n</i> -Butyl acetate	Water	90.2	26.7
<i>sec</i> -Butyl acetate	Water	86.6	19.4
Isobutyl acetate	Water	87.4	–
<i>n</i> -Butyl acetate	<i>n</i> -Butanol	117.2	47
<i>sec</i> -Butyl acetate	<i>sec</i> -Butanol	99.6	86.3

Uses. Ethyl acetate is a common solvent for coatings, adhesives, ink, cosmetics, and film base. Specialty chemicals and pharmaceutical industries use ethyl acetate as a solvent for synthesis. Coffee is occasionally decaffeinated with ethyl acetate in an extraction process.

10.2.3. Butyl Acetate

Properties. All four of the esters, *n*-butyl [123-86-4], *sec*-butyl [105-46-4], isobutyl [110-19-0], and *tert*-butyl acetate [540-88-5], are colorless liquids with pleasant odors. Azeotropic data for the butyl acetates are given in Tables 8 and 9 [5]. Other properties are listed in Table 7.

Production. Esterification of butanol and acetic acid produces butyl acetate. The catalyst is sulfuric acid. The removal of water by azeotropic separation forces the reaction to completion. The acid catalyst is neutralized and the ester purified by distillation [8].

Uses. Butyl acetate is used primarily in coatings. It is a good solvent with low volatility. The lacquer and enamel industries employ butyl acetate as a solvent for making acyclic polymers, vinyl resins, and nitrocellulose. Other industries utilizing the acetate as solvent include printing, photographic, adhesives, extraction and pharmaceutical.

10.2.4. 2-Ethylhexyl Acetate

2-Ethylhexyl acetate is prepared by esterification of 2-ethyl-1-hexanol with acetic acid with the aid

of an acid catalyst. Distillation with a low-boiling azeotropic solvent removes water from the reaction. The ester is used in lacquers, in silk-screen inks, and in paints as a coalescing agent. Properties are listed in Table 7.

10.2.5. Other Esters

Properties of some other esters are given in Table 7. Most esters are colorless liquids with a mild fruity smell. The esters are used as solvents for making cellulose and elastomers [178].

10.3. Acetyl Chloride

Properties. Acetyl chloride [75-36-5] M_r 78.5, n_D^{20} 1.3871, d_4^{20} 1.1051, bp 51.8°C, mp - 112.86 °C is a colorless, corrosive liquid. Acetyl chloride reacts with moist air to produce hydrogen chloride and acetic acid.

Production. The normal industrial method involves reaction of acetic anhydride [108-24-7] with anhydrous hydrogen chloride [7647-01-0] [179, 180]. On the laboratory scale, it can be produced from acetic acid and reagents such as thionyl chloride [7719-09-7], phosphorus trichloride [7719-12-2], or phosphorus pentachloride [10026-13-8] [181].

Acetyl chloride is normally consumed at the site of generation since transportation and storage are difficult. Glass, enamel, porcelain, clay, and polytetrafluoroethylene are suitable materials for handling acetyl chloride.

Uses. Acetyl chloride is an efficient acetylating agent for alcohols and amines to produce esters and amides. It is important in the synthesis of dyes and pharmaceuticals. Acetyl chloride is used in the Friedel – Craft acylation of benzene to yield acetophenone.

10.4. Amides

10.4.1. Acetamide

Properties. Acetamide [60-35-5], CH_3CONH_2 , M_r 59.07, mp 81.5 °C, bp 222°C,

d^{20} 1.161, forms deliquescent hexagonal crystals that are odorless when pure. Acetamide is soluble in water and low molecular mass alcohols.

Production. Acetamide can be produced by several methods. Ammonia reacts vigorously with acetyl halides or acetic anhydride to produce acetamide. Alkyl acetates also react with ammonia to yield acetamide. Dehydration of ammonium acetate is the standard procedure for preparation of acetamide. Finally, acetonitrile is hydrolyzed to yield acetamide in the presence of an acid or base catalyst. Metal catalysts [183, 184] and biocatalysts [185] are claimed to catalyze the hydrolysis of acetonitrile. This method of acetamide production is popular because acetonitrile is a byproduct of acrylonitrile production.

Uses. Acetamide is used as a solvent and as a plasticizer.

10.4.2. *N,N*-Dimethylacetamide

Properties. *N,N*-Dimethylacetamide, [127-19-5], $CH_3CON(CH_3)_2$, M_r 87.1, mp - 20 °C, bp 165.5 °C, d^{20} 0.943, is a colorless liquid which is soluble in a wide variety of solvents.

Production. *N,N*-Dimethylacetamide is prepared by reaction of dimethylamine with acetic acid, acetic anhydride, or acetate esters. Heating dimethylamine acetate with [186, 187] or without [188] a catalyst affords *N,N*-dimethylacetamide. Reaction of dimethylamine with acetate esters requires a catalyst; sodium methoxide is typically used.

Uses. *N,N*-dimethylacetamide is an excellent solvent and often acts as a catalyst in halogenation, cyclization, and alkylation reactions. *N,N*-Dimethylacetamide is used in the spinning of polyacrylonitrile and as a solvent in the processing of other polymers. *N,N*-dimethylacetamide lithium chelate complexes intercalate cationic sites in layered silicates [189].

10.5. Phenylacetic Acid

Properties. Phenylacetic acid [103-82-2], $C_6H_5CH_2CO_2H$, M_r 136.14, bp 265.5 °C, mp

78 °C, $d^{79.8}$ 1.0809, forms white leaflets on vacuum distillation. It dissolves in hot water but is only slightly soluble in cold water.

Production. Hydrolysis of benzyl cyanide or carbonylation [190] of benzyl halides or alcohols produces phenylacetic acid [191].

Uses. Phenylacetic acid is a starting material in the synthesis of synthetic perfumes and cosmetics [192]. It is used in the synthesis of penicillin G to stimulate benzylpenicillinase in *E. Coli*. Penicillin G, after extraction from the culture, is converted to 6-aminopenicillanic acid and phenylacetic acid.

11. Economic Aspects [1]

In 2008 total world acetic acid capacity and total world production were both ca. 10.6×10^6 t/a.

In 1996, North America was the region with the greatest acetic acid production at ca. 36 % of the world total. Western Europe was second with ca. 24 % followed by Japan at 15 % and Eastern Asia with 14 %. In 2007 about 55 % of total production capacity was outside the United States, Western Europe, and Japan, with the majority in Asia.

The largest end uses of acetic acid are for the manufacture of vinyl acetate, acetic anhydride, acetate esters, monochloroacetic acid, and as a solvent in the production of dimethyl terephthalate and terephthalic acid. Figure 8 provides a detailed summary of acetic acid end uses. Vinyl acetate is by far the most significant end use for acetic acid. About 33 % of world production of acetic acid in 2008 was used in the manufacture of vinyl acetate, followed by terephthalic acid, acetic anhydride, and acetate esters.

There is little doubt that the technology of the future is methanol carbonylation. In 1972, low-pressure methanol carbonylation in the United States accounted for only 10 % of the total acetic acid capacity, whereas in 1982 the share had increased to 40 %. By 1993, 46 % of the acetic acid was produced by methanol carbonylation. Over 90 % of all new acetic acid is manufactured by low-pressure methanol carbonylation technology.

BP Chemicals purchased the technology and license rights to the Monsanto methanol carbonylation process in 1986 and has continued to license in joint ventures this high-reaction-water process. Technology improvements have been made in the rhodium-catalyzed carbonylation process since this process was first implemented commercially [52]. Celanese in the early 1980s departed from the Monsanto high-water technology to develop a proprietary low-reaction-water process. BP also has developed a low-reaction-water technology based on iridium called Cativa that has several advantages over the rhodium-catalyzed high-reaction-water process [55] originally developed by Monsanto. These developments, as well as others, will most likely ensure that in the future the low-pressure methanol carbonylation processes will remain the most economical routes to manufacture acetic acid.

Acetic acid from low-pressure methanol carbonylation is gradually replacing the more expensive acetic acid produced by the oxidation of acetaldehyde, butane, and naphtha and by high-pressure methanol carbonylation. The oxidation routes to acetic acid in most cases are not competitive with low-pressure methanol carbonylation. Acetaldehyde oxidation units are only economically viable provided an acetic acid producer has a captive source of acetaldehyde. Similarly, *n*-butane or naphtha oxidation processes are not competitive with low-pressure methanol carbonylation unless byproduct credits are considered. As a result, many high-cost acetic acid units have ceased operation, such as the acetaldehyde oxidation processes of Celanese in Clear Lake and Bay City Texas, and a similar process of Eastman Chemical in Kingsport, Texas. Additionally, the butane oxidation plant operated by Union Carbide at Brownsville, Texas, and the high-pressure methanol carbonylation plant of Borden in Geismar, Louisiana, have ceased operation.

12. Toxicology and Occupational Health

Acetic acid has a pK_a of 4.5. The acid is not as strong as mineral acids or formic acid. However, its corrosiveness justifies caution in handling.

Table 10 lists exposure limits for acetic acid and derivatives [194].

Table 10. Exposure limits to acetic acid and its derivatives [93, 94]

Substance	TLV					
	TWA		STEL		MAK	
	ppm	mg/m ³	ppm	mg/m ³	mL/m ³	mg/m ³
Acetic acid	10	25	15	37	10	25
<i>n</i> -Butyl acetate	150	713	200	950	200	950
<i>sec</i> -Butyl acetate	200	950			200	950
Dimethylacetamide (skin)	10	36			10	35
Ethyl acetate	400	1400			400	1400
Methyl acetate	200	606	250	757	200	610

When humans ingest acetates, the esters are hydrolyzed readily to the corresponding alcohols and carboxylic acids. A study using radioactive labeling shows that the liver and brain cholesterol incorporate acetic acid [195]. No cumulative toxicity has been reported.

Dilute acid with 5% acetic acid such as vinegar can cause irritation to human mucous membranes. Vinegar contains 3 – 6% acid. Persons of older than two years can take as much as 2.1 g daily. However, the dilute acid damages skin more severely than other mineral acids because it is miscible with lipids.

Acetic acid irritates the eyes, nose, and throat above 10 ppm. Repeated exposure to 26 ppm for ten days causes adverse effects. Over 100 ppm, the acid may even damage organs as described above.

Concentrated acid can damage skin severely. Avoid exposure to glacial acetic acid or inhaling vapor. In case of contact, wash the exposed area with plenty of water. Therefore, handling of the acid requires caution.

Oral ingestion of the acid causes pain in the digestive tract and in the mouth. It may lead to vomiting, and respiratory and circulatory distress. If the person is conscious, wash the mouth with water and consult physicians.

Acetic acid has a low flash point of 39 °C [196]. It is readily combustible with an autoignition point of 516 °C. Fortunately, the acid lowers its flammability significantly when mixed with water. Beyond 56%, the flash point is no longer a danger [197].

Organic acetates do not cause severe damage unless high exposure occurs. The TLVs vary from 5 to 400 ppm [198]. The LD₅₀ for small mammals range from 0.4 to 16 g/kg. The toxicity

of the esters decreases as the molecular mass increases from C₁ to C₄. The LD₅₀ of isoamyl acetate (7.42 g/kg) is twice that of methyl acetate (3.7 g/kg). However, ingestion or absorption of methyl acetate poses a hazard since the ester is converted to methanol.

Acetates irritate the mucous membrane slightly. When ingested or absorbed, esters are readily hydrolyzed to the corresponding alcohols and carboxylic acids. Some volatile esters act as asphyxiants and narcotics.

Ethyl acetate has an LD₅₀ of 4.97 g/kg in the rabbit. The toxicity of acetates is usually in the range of 100 – 250 ppm. Ethyl acetate has the highest PEL of 500 ppm. Humans can tolerate up to 400 ppm before nose and throat irritation.

n-Butyl acetate differs from its isomers. When tested with rats, *n*-butyl acetate has an oral LD₅₀ of 14 mg/kg. For humans, irritation in the throat starts at an exposure of 200 ppm [194]. Severe eye and nose irritation occurs at 300 ppm. *sec*-Butyl acetate poses less hazard than its normal isomer, with less odor and less irritation. The lethal dose for *sec*-butyl acetate in rabbits is 4.8 mg/kg.

Acetyl chloride is harmful if swallowed, inhaled, or absorbed through the skin. Target areas include the peripheral nervous system, sense organs, CNS (behavior), lungs, thorax and respiratory system. Acetyl chloride reacts with moist air to produce hydrogen chloride and acetic acid.

Amides are more hazardous than esters. Acetamide causes skin and eye irritation. It is also irritating to the mucous membranes and the upper respiratory tract. It is considered a carcinogen and has been shown to alter DNA in mouse and rat embryos. Methylacetamide has teratogenic

and neoplastic potential. *N,N*-Dimethylacetamide causes hallucinogenic effects similar to those of LSD at doses of 400 mg/kg [199]. *N,N*-dimethylacetamide overexposure has led to reproductive disorders in laboratory animals. Target organs include the liver, kidney, and CNS. For humans, damage to the liver occurs at the exposure level of 20 – 25 ppm. The recommended TLV is 10 ppm without skin exposure.

Phenylacetic acid is irritating to the eyes, skin, mucous membranes, and upper respiratory system.

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