ACRYLIC ACID AND DERIVATIVES

1. Introduction

The term acrylates includes derivatives of both acrylic ($CH_2{=}CHCOOH$) and methacrylic acids ($CH_2{=}C(CH_3)COOH$). This article discusses the preparation, properties, and reactions of acrylic acid monomers only (see METHACRYLIC ACID AND DERIVATIVES). Acrylic acid (propenoic acid) was first prepared in 1847 by air oxidation of acrolein (1). Interestingly, after use of several other routes over the past half century, it is this route, using acrolein from the catalytic oxidation of propylene, that is currently the most favored industrial process. Polymerization of acrylic esters has been known for just over a century (2). However, it was not until 1930 that the technical difficulties of their manufacture and polymerization were overcome (3). The rate of consumption of acrylates grew between 10 and 20% annually during the late 1970s. Growth fluctuated with the economy in the early 1980s with some announced capacity increases being delayed until later in the decade. Although growth in the ester markets has dropped appreciably, new applications for polymers of acrylic acid in the superabsorbent and detergent fields surged in the late 1980s. U. S. demand for acrylic acid is expected to grow at a 4.0% annual rate, and reach 1.2×10^9 kg by 2004.

Acrylates are primarily used to prepare emulsion and solution polymers. The emulsion polymerization process provides high yields of polymers in a

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form suitable for a variety of applications. Acrylate polymer emulsions were first used as coatings for leather in the early 1930s and have found wide utility as coatings, finishes, and binders for leather, textiles, and paper. Acrylate emulsions are used in the preparation of both interior and exterior paints, floor polishes, and adhesives. Solution polymers of acrylates, frequently with minor concentrations of other monomers, are employed in the preparation of industrial coatings. Polymers of acrylic acid can be used as superabsorbents in disposable diapers, as well as in formulation of superior, reduced-phosphate-level detergents.

The polymeric products can be made to vary widely in physical properties through controlled variation in the ratios of monomers employed in their preparation, cross-linking, and control of molecular weight. They share common qualities of high resistance to chemical and environmental attack, excellent clarity, and attractive strength properties (see ACRYLIC ESTER POLYMERS). In addition to acrylic acid itself, methyl, ethyl, butyl, isobutyl, and 2-ethylhexyl acrylates are manufactured on a large scale and are available in better than 98–99% purity (4). They usually contain 10–200 ppm of hydroquinone monomethyl ether as polymerization inhibitor.

2. Physical Properties

Physical properties of acrylic acid and representative derivatives appear in Table 1. Table 2 gives selected properties of commercially important acrylate esters, and Table 3 lists the physical properties of many acrylic esters.

Acrylic acid is a moderately strong carboxylic acid. Its dissociation constant is 5.5×10^{-5}. Vapor pressure as a function of temperature is given in Table 4 for acrylic acid and four important esters (4,16–18). The lower esters form azeotropes both with water and with their corresponding alcohols.

Table 1. **Physical Properties of Acrylic Acid Derivatives**

Property	Acrylic acid	Acrolein	Acrylic anhydride	Acryloyl chloride	Acrylamide
molecular formula	$C_3H_4O_2$	C_3H_4O	$C_6H_6O_3$	C_3H_3OCl	C_3H_5ON
CAS Registry Number	[79-10-7]	[107-02-8]	[2051-76-5]	[814-68-6]	[79-06-1]
melting point, °C	13.5	−88			84.5
boiling point[a], °C	141	52.5	38[b]	75	125[c]
refractive index[d], n_D	1.4185[e]	1.4017	1.4487	1.4337	
flash point, Cleveland open cup, °C	68				
density[d], g/mL	1.045[e]	0.838		1.113	1.122[f]

[a] At 101.3 kPa = 1 atm unless otherwise noted.
[b] At 0.27 kPa.
[c] At 16.6 kPa.
[d] At 20°C, unless otherwise noted.
[e] At 25°C.
[f] At 30°C.

Table 2. **Properties of Commercially Important Acrylate Esters**[a]

Property	Methyl	Ethyl	n-Butyl	Isobutyl	2-Ethylhexyl
solubility at 23°C, parts per 100 of solvent					
in water	5	1.5	0.2	0.2	0.01
of water in ester	2.5	1.5	0.7	0.6	0.15
heat of vaporization, kJ/g[b]	0.39	0.35	0.19	0.30	0.25
specific heat, J/g·C[b]	2.00	1.97	1.93	1.93	1.93
boiling points[c] of azeotropes					
with water, °C	71	81.1	94.5		
water content, %	7.2	15	40		
with methanol, °C	62.5	64.5			
methanol content, %	54	84.4			
with ethanol, °C	73.5	77.5			
ethanol content, %	42.4	72.7			
with n-butanol, °C			119		
butanol content, %			89		
heat of polymerization, kJ/mol[b]	78.7	77.8	77.4		

[a] Refs. 4,5

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

[c] At 101.3 kPa = 1 atm.

3. Reactions

Acrylic acid and its esters may be viewed as derivatives of ethylene, in which one of the hydrogen atoms has been replaced by a carboxyl or carboalkoxyl group. This functional group may display electron-withdrawing ability through inductive effects of the electron-deficient carbonyl carbon atom, and electron-releasing effects by resonance involving the electrons of the carbon–oxygen double bond. Therefore, these compounds react readily with electrophilic, free-radical, and nucleophilic agents.

3.1. Carboxylic Acid Functional Group Reactions.

Polymerization is avoided by conducting the desired reaction under mild conditions and in the presence of polymerization inhibitors. Acrylic acid undergoes the reactions of carboxylic acids and can be easily converted to salts, acrylic anhydride, acryloyl chloride, and esters (16,17).

Salts are made by reaction of acrylic acid with an appropriate base in aqueous medium. They can serve as monomers and comonomers in water-soluble or water-dispersible polymers for floor polishes and flocculants.

Acrylic anhydride is formed by treatment of the acid with acetic anhydride or by reaction of acrylate salts with acryloyl chloride. *Acryloyl chloride* is made by reaction of acrylic acid with phosphorous oxychloride, or benzoyl or thionyl chloride. Neither the anhydride nor the acid chloride is of commercial interest.

Esters. Most acrylic acid is used in the form of its methyl, ethyl, and butyl esters. Specialty monomeric esters with a hydroxyl, amino, or other functional group are used to provide adhesion, latent cross-linking capability, or different solubility characteristics. The principal routes to esters are direct esterification with alcohols in the presence of a strong acid catalyst such as sulfuric acid, a

Table 3. **Physical Properties of Acrylic Esters[a], $CH_2{=}CHCOOR$**

Compound	Molecular formula	CAS Registry Number	Boling point		Refractive index n^{20}_{D}	Density d^{20}_{4}
			°C	kPa[b]		
n-Alkyl esters[c]						
methyl	$C_4H_6O_2$	[96-33-3]	80	101	1.4040	0.9535
ethyl	$C_5H_8O_2$	[140-88-5]	43	13.7	1.4068	0.9234
propyl	$C_6H_{10}O_2$	[925-60-0]	44	5.3	1.4130	0.9078
butyl	$C_7H_{12}O_2$	[141-32-2]	35	1.1	1.4190	0.8998
pentyl	$C_8H_{14}O_2$	[2998-23-4]	48	0.9	1.4240	0.8920
hexyl	$C_9H_{16}O_2$	[2499-95-8]	40	0.15	1.4280	0.8882
heptyl	$C_{10}H_{18}O_2$	[2499-58-3]	57	0.13	1.4311	0.8846
octyl	$C_{11}H_{20}O_2$	[2499-59-4]	57	0.007	1.4350	0.8810
nonyl	$C_{12}H_{22}O_2$	[2664-55-3]	76	0.03	1.4375	0.8785
decyl	$C_{13}H_{24}O_2$	[2156-96-9]	120	0.67	1.4400	0.8781
dodecyl	$C_{15}H_{28}O_2$	[2156-97-0]	120	0.11	1.4440	0.8727
tetradecyl	$C_{17}H_{32}O_2$	[21643-42-5]	138	0.05	1.4468	0.8700
hexadecyl	$C_{19}H_{36}O_2$	[13402-02-3]	170	0.20	1.4470 (30°C)	0.8620 (30°C)
Secondary and branched-chain alkyl esters[d]						
isopropyl	$C_6H_{10}O_2$	[689-12-3]	52	13.7	1.4060	0.8932
isobutyl	$C_7H_{12}O_2$	[106-62-8]	62	6.7	1.4150	0.8896
sec-butyl	$C_7H_{12}O_2$	[2998-08-5]	60	6.7	1.4140	0.8914
2-ethylhexyl	$C_{11}H_{20}O_2$	[103-11-7]	85	1.07	1.4365	0.8852
Esters of olefinic alcohols[e]						
allyl	$C_6H_8O_2$	[999-55-3]	47	5.33	1.4320	0.9441
2-methylallyl	$C_7H_{10}O_2$	[818-67-7]	68	6.67	1.4372	0.9285
Aminoalkyl esters[f]						
2-(dimethylamino)-ethyl	$C_7H_{13}O_2N$	[2439-35-2]	61	1.47	0.9434	1.4375
2-(diethylamino)ethyl	$C_9H_{17}O_2N$	[2426-54-2]	70	0.67	0.9251	1.4425
Esters of ether alcohols[c]						
2-methoxyethyl	$C_6H_{10}O_3$	[3121-67-7]	59	1.60	1.4272	1.0131
2-ethoxylethyl	$C_8H_{12}O_3$	[106-74-1]	78	3.07	1.4282	0.9819
Cycloalkyl esters[g]						
cyclohexyl	$C_9H_{14}O_2$	[3066-71-5]	75	1.47	1.4600	0.9796
4-methylcyclohexyl	$C_{10}H_{16}O_2$	[16491-65-9]	55	0.27	1.4550	0.9537
Esters of halogenated alcohols[h]						
2-bromoethyl	C_5H_7Br	[4823-47-6]	53	5	1.4770	1.4774
2-chloroethyl	C_5H_7Cl	[2206-89-5]	74	29	1.4477	
Glycol diacrylates[i]						
ethylene glycol (monoester)	$C_5H_8O_3$	[818-61-1]	40	0.001	1.4482 (25°C)	
ethylene glycol	$C_8H_{10}O_4$	[2274-11-5]	70	0.13	1.4529	
propylene glycol	$C_9H_{12}O_4$	[999-61-1]	63	0.04	1.4470	
1,3-propanediol	$C_9H_{12}O_4$	[25151-33-1]	65	<0.13	1.4529	
1,4-butanediol	$C_{10}H_{14}O$	[31442-13-4]	83	0.04	1.4538	
diethylene glycol	$C_{10}H_{14}O_5$	[4074-88-8]	94	0.03	1.4572	
1,5-pentanediol	$C_{11}H_{16}O_4$	[36840-85-4]	94	0.04	1.4551	
1,10-decanediol	$C_{16}H_{26}O_4$	[13048-45-5]	145	0.01		

[a] In most cases, the references include additional examples of the class alcohols. Nitroalkyl esters are known (6,7).

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] Ref. 8

[d] Ref. 9.

[e] Ref. 10.

[f] Ref. 11.

[g] Ref. 12.

[h] Refs. 13–15.

[i] Ref. 5.

Table 4. **Vapor Pressures of Acrylic Acid and Important Esters[a], kPa[b]**

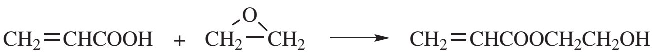
Temperature, °C	Acrylic acid	Methyl acrylate	Ethyl acrylate	Butyl acrylate	2-Ethylhexyl acrylate
−20		0.85	0.31		
−10		1.72	0.61		
0		3.12	1.16	0.15	
10		5.40	2.20	0.28	
20		9.09	3.93	0.53	
30	0.8	14.5	6.73	0.97	
40	1.4	22.7	10.9	1.71	
50	2.4	34.0	16.8	2.84	0.13
60	4.0	49.6	25.3	4.53	0.25
70	6.6	70.7	37.3	7.13	0.44
80	10		53.3	10.9	0.75
90	16		74.7	16.0	1.23
100	24			23.06	1.97
110	35			32.8	3.06
120	49			45.6	4.62
130	69			61.9	6.79
140	99			82.3	10.1
150					14.4
160					20.0
170					28.0
180					37.3
190					50.0
200					65.6
210					85.3

[a] Ref. 4.

[b] To convert kPa to mm Hg, multiply by 7.5.

soluble sulfonic acid, or sulfonic acid resins; addition to alkylene oxides to give hydroxyalkyl acrylic esters; and addition to the double bond of olefins in the presence of strong acid catalyst (19,20) to give ethyl or secondary alkyl acrylates.

$$CH_2{=}CHCOOH + ROH \xrightarrow{H^+} CH_2{=}CHCOOR + H_2O$$

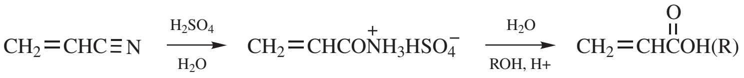


$$CH_2{=}CHCOOH + \overset{O}{CH_2{-}CH_2} \longrightarrow CH_2{=}CHCOOCH_2CH_2OH$$

$$CH_2{=}CHCOOH + CH_2{=}CH_2 \xrightarrow{H^+} CH_2{=}CHCOOCH_2CH_3$$

Acrylic esters may be saponified, converted to other esters (particularly of higher alcohols by acid catalyzed alcohol interchange), or converted to amides by aminolysis. Transesterification is complicated by the azeotropic behavior of lower acrylates and alcohols but is useful in preparation of higher alkyl acrylates.

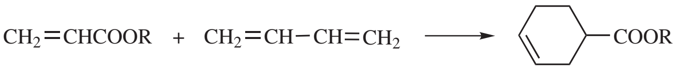
Amides. Reaction of acrylic acid with ammonia or primary or secondary amines forms amides. However, acrylamide (qv) is better prepared by controlled hydrolysis of acrylonitrile (qv). Esters can be obtained by carrying out the nitrile hydrolysis in the presence of alcohol.



$$CH_2{=}CHC{\equiv}N \xrightarrow[H_2O]{H_2SO_4} CH_2{=}CHCO\overset{+}{N}H_3HSO_4^- \xrightarrow[ROH,\ H+]{H_2O} CH_2{=}CH\overset{\overset{O}{\|}}{C}OH(R)$$

3.2. Unsaturated Group Reactions. In addition to a comprehensive review of these reactions (16), there are excellent texts (17,18). Free-radical-initiated polymerization of the double bond is the most common reaction and presents one of the more troublesome aspects of monomer manufacture and purification.

Substituted ring compounds are formed readily by Diels-Alder reactions.



Additions. Halogens, hydrogen halides, and hydrogen cyanide readily add to acrylic acid to give the 2,3-dihalopropionate, 3-halopropionate, and 3-cyanopropionate, respectively (21).

On storage or at elevated temperatures, acrylic acid dimerizes to give 3-acryloxypropionic acid [24615-84-7], $C_6H_8O_4$.

$$2\ CH_2{=}CHCOOH \longrightarrow CH_2{=}CHCOOCH_2CH_2COOH$$

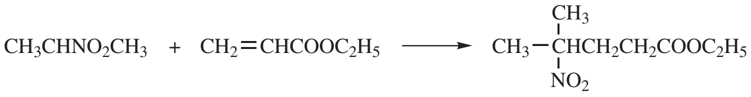
Although the reaction is second order in acrylic acid concentration, the rate of dimer formation for neat acrylic acid available commercially is quite adequately expressed by

$$\text{rate} = 3.58 \times 10^{17}\exp(-10,500/T)$$

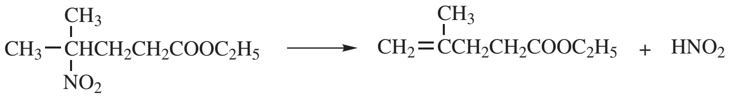
over the first several percent conversion (5), where rate is in ppm/day and T is the Kelvin temperature. Since this rate is approximately 100 ppm/day at 20°C, significant dimer can build up on prolonged storage. The reaction is accelerated by addition of strong acids, bases, or large amounts of water (several wt %). However, water at concentrations as low as 0.1–0.2 wt %, present in commercially available acrylic acid, has negligible effect on dimer formation (5,22). Continuation of this reaction leads to a distribution of polyester oligomers formed by successive additions across the double bond (5). Acrylic acid can be regenerated by thermal or acid catalyzed cracking of these oligomers (23). Cracking of the corresponding esters gives acrylic acid and acrylic ester.

$$CH_2{=}CHCOOCH_2CH_2COOR \longrightarrow CH_2{=}CHCOOH + CH_2{=}CHCOOR$$

Michael condensations are catalyzed by alkali alkoxides, tertiary amines, and quaternary bases and salts. Active methylene compounds and aliphatic nitro compounds add to form β-substituted propionates. These addition reactions are frequently reversible at high temperatures. Exceptions are the tertiary nitro adducts which are converted to olefins at elevated temperatures (24).



$$\mathrm{CH_3CHNO_2CH_3} + \mathrm{CH_2{=}CHCOOC_2H_5} \longrightarrow \mathrm{CH_3{-}\underset{NO_2}{\overset{CH_3}{C}}HCH_2CH_2COOC_2H_5}$$



$$\mathrm{CH_3{-}\underset{NO_2}{\overset{CH_3}{C}}HCH_2CH_2COOC_2H_5} \longrightarrow \mathrm{CH_2{=}\overset{CH_3}{C}CH_2CH_2COOC_2H_5} + \mathrm{HNO_2}$$

The addition of alcohols to form the 3-alkoxypropionates is readily carried out with strongly basic catalyst (25). If the alcohol groups are different, ester interchange gives a mixture of products. Anionic polymerization to oligomeric acrylate esters can be obtained with appropriate control of reaction conditions. The 3-alkoxypropionates can be cleaved in the presence of acid catalysts to generate acrylates (26). Development of transition-metal catalysts for carbonylation of olefins provides routes to both 3-alkoxypropionates and 3-acryl-oxypropionates (27,28). Hence these are potential intermediates to acrylates from ethylene and carbon monoxide.

Additions of mercaptans with alkaline catalysts give 3-alkylthiopropionates (29). In the case of hydrogen sulfide, the initially formed 3-mercaptopropionate reacts with a second molecule of acrylate to give a 3,3′-thiodipropionate (30,31).

$$\mathrm{H_2S} + 2\ \mathrm{CH_2{=}CHCOOR} \longrightarrow \mathrm{S(CH_2CH_2COOR)_2}$$

Polythiodipropionic acids and their esters are prepared from acrylic acid or an acrylate with sulfur, hydrogen sulfide, and ammonium polysulfide (32). These polythio compounds are converted to the dithio analogs by reaction with an inorganic sulfite or cyanide.

$$2\ \mathrm{CH_2{=}CHCOOCH_3} + \mathrm{S}_x + \mathrm{H_2S} \xrightarrow{\mathrm{(NH_4)_2S}_x}$$

$$\mathrm{S}_x\mathrm{(CH_2CH_2COOCH_3)_2} \xrightarrow{\mathrm{NaCN}} \mathrm{CH_3OOCCH_2CH_2SSCH_2CH_2COOCH_3}$$

Ammonia and amines add to acrylates to form β-aminopropionates, which add easily to excess acrylate to give tertiary amines. The reactions are reversible (33).

$$\mathrm{NH_3} + \mathrm{CH_2{=}CHCOOR} \longrightarrow \mathrm{H_2NCH_2CH_2COOR} \xrightarrow{\mathrm{CH_2{=}CHCOOR}}$$

$$\mathrm{HN(CH_2CH_2COOR)_2} \xrightarrow{\mathrm{CH_2{=}CHCOOR}} \mathrm{N(CH_2CH_2COOR)_3}$$

Aqueous ammonia and acrylic esters give tertiary amino esters, which form the corresponding amide upon ammonolysis (34). Modern methods of molecular quantum modeling have been applied to the reaction pathway and energetics for several nucleophiles in these Michael additions (35,36).

Acrylic esters dimerize to give the 2-methylene glutaric acid esters catalyzed by tertiary organic phosphines (37) or organic phosphorous triamides, phosphonous diamides, or phosphinous amides (38). Yields of 75–80% dimer, together with 15–20% trimer, are obtained. Reaction conditions can be varied to obtain high yields of trimer, tetramer, and other polymers.

4. Manufacture

Various methods for the manufacture of acrylates are summarized in Figure 1, showing their dependence on specific raw materials. For a route to be commercially attractive, the raw material costs and utilization must be low, plant investment and operating costs not excessive, and waste disposal charges minimal.

After development of a new process scheme at laboratory scale, construction and operation of pilot-plant facilities to confirm scale-up information often require two or three years. An additional two to three years is commonly required for final design, fabrication of special equipment, and construction of the plant. Thus, projections of raw material costs and availability five to ten years into the future become important in adopting any new process significantly different from the current technology.

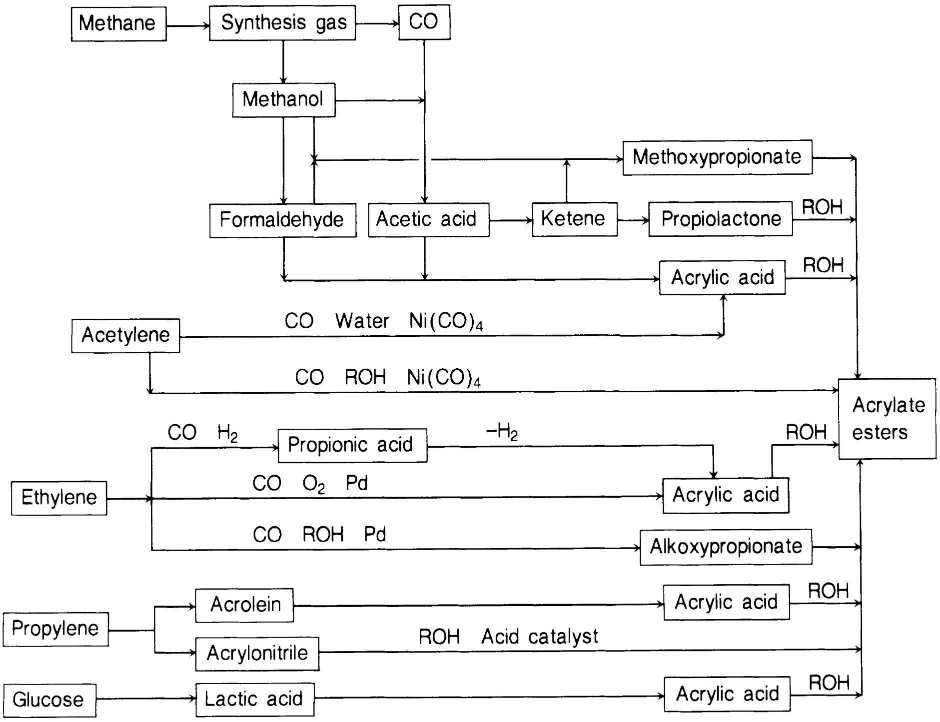


Fig. 1. Acrylate manufacturing technologies.

In the 1980s cost and availability of acetylene have made it an unattractive raw material for acrylate manufacture as compared to propylene, which has been readily available at attractive cost (see ACETYLENE-DERIVED CHEMICALS). As a consequence, essentially all commercial units based on acetylene, with the exception of BASF's plant at Ludwigshafen, have been shut down. All new capacity recently brought on stream or announced for construction uses the propylene route. Rohm and Haas Co. has developed an alternative method based on alkoxycarbonylation of ethylene, but has not commercialized it because of the more favorable economics of the propylene route.

Propylene requirements for acrylates remain small compared to other chemical uses (polypropylene, acrylonitrile, propylene oxide, 2-propanol, and cumene for acetone and phenol). Hence, cost and availability are expected to remain attractive and new acrylate capacity should continue to be propylene-based until after the turn of the century.

4.1. Propylene Oxidation. The propylene oxidation process is attractive because of the availability of highly active and selective catalysts and the relatively low cost of propylene. The process proceeds in two stages giving first acrolein and then acrylic acid (39) (see ACROLEIN AND DERIVATIVES).

$$CH_2{=}CHCH_3 + O_2 \longrightarrow CH_2{=}CHCHO + H_2O$$

$$CH_2{=}CHCHO + \frac{1}{2}\,O_2 \longrightarrow CH_2{=}CHCOOH$$

Single-reaction-step processes have been studied. However, higher selectivity is possible by optimizing catalyst composition and reaction conditions for each of these two steps (40,41). This more efficient utilization of raw material has led to two separate oxidation stages in all commercial facilities. A two-step continuous process without isolation of the intermediate acrolein was first described by the Toyo Soda Company (42). A mixture of propylene, air, and steam is converted to acrolein in the first reactor. The effluent from the first reactor is then passed directly to the second reactor where the acrolein is oxidized to acrylic acid. The products are absorbed in water to give about 30–60% aqueous acrylic acid in about 80–85% yield based on propylene.

Japan Catalytic Chemical Co. (43) and Mitsubishi Petrochemical Co. (44) offer licenses to their acrylate manufacturing technology (including high quality catalysts). Thus, although most manufacturers have also developed their own catalyst and process technologies, many have also taken licenses from these companies and either constructed entire plants based on those disclosures or combined that technology with their own developments for their operating plants.

Catalysts. Catalyst performance is the most important factor in the economics of an oxidation process. It is measured by activity (conversion of reactant), selectivity (conversion of reactant to desired product), rate of production (production of desired product per unit of reactor volume per unit of time), and catalyst life (effective time on-stream before significant loss of activity or selectivity).

Early catalysts for acrolein synthesis were based on cuprous oxide and other heavy metal oxides deposited on inert silica or alumina supports (39).

Later, catalysts more selective for the oxidation of propylene to acrolein and acrolein to acrylic acid were prepared from bismuth, cobalt, iron, nickel, tin salts, and molybdic, molybdic phosphoric, and molybdic silicic acids. Preferred second-stage catalysts generally are complex oxides containing molybdenum and vanadium. Other components, such as tungsten, copper, tellurium, and arsenic oxides, have been incorporated to increase low temperature activity and productivity (39,45,46).

Catalyst performance depends on composition, the method of preparation, support, and calcination conditions. Other key properties include, in addition to chemical performance requirements, surface area, porosity, density, pore size distribution, hardness, strength, and resistance to mechanical attrition.

Patents claiming specific catalysts and processes for their use in each of the two reactions have been assigned to Japan Catalytic (45,47–49), Sohio (50), Toyo Soda (51), Rohm and Haas (52), Sumitomo (53), BASF (54), Mitsubishi Petrochemical (56,57), Celanese (55), and others. The catalysts used for these reactions remain based on bismuth molybdate for the first stage and molybdenum vanadium oxides for the second stage, but improvements in minor component composition and catalyst preparation have resulted in yields that can reach the 85–90% range and lifetimes of several years under optimum conditions. Since plants operate under more productive conditions than those optimum for yield and life, the economically most attractive yields and productive lifetimes may be somewhat lower.

Oxidation Step. A review of mechanistic studies of partial oxidation of propylene has appeared (58). The oxidation process flow sheet (Fig. 2) shows equipment and typical operating conditions. The reactors are of the fixed-bed

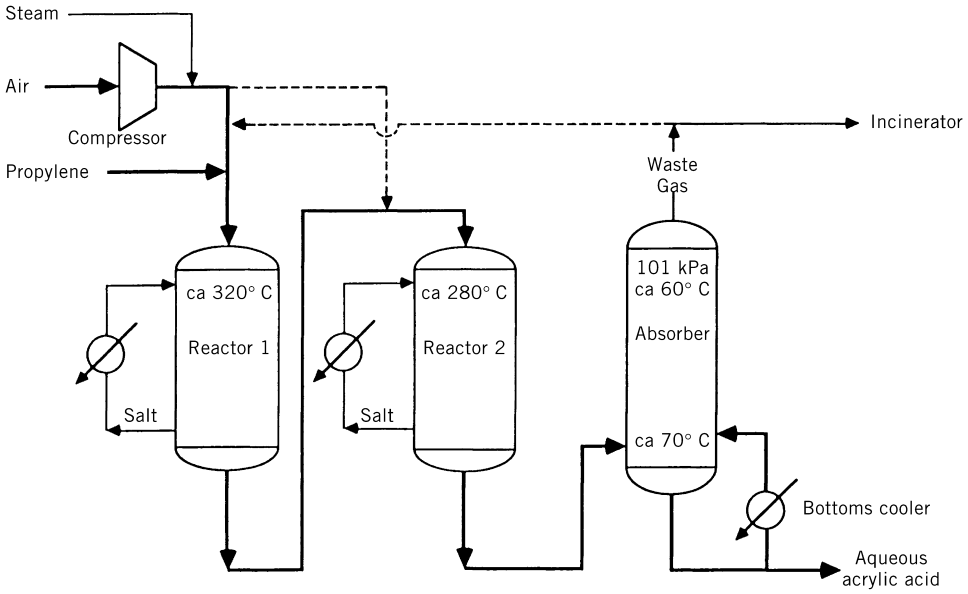


Fig. 2. Oxidation process. To convert kPa to mm Hg, multiply by 7.5.

shell-and-tube type (about 3–5 m long and 2.5 cm in diameter) with a molten salt coolant on the shell side. The tubes are packed with catalyst, a small amount of inert material at the top serving as a preheater section for the feed gases. Vaporized propylene is mixed with steam and air and fed to the first-stage reactor. The feed composition is typically 5–7% propylene, 10–30% steam, and the remainder air (or a mixture of air and absorber off-gas) (56,57,59,60).

The preheated gases react exothermically over the first-stage catalyst with the peak temperature in the range of 330–430°C, depending on conditions and catalyst selectivity. The conversion of propylene to waste gas (carbon dioxide and carbon monoxide) is more exothermic than its conversion to acrolein. At the end of the catalyst bed the temperature of the mixture drops toward that of the molten salt coolant.

If necessary, first-stage reactor effluent may be further cooled to 200–250°C by an interstage cooler to prevent homogeneous and unselective oxidation of acrolein taking place in the pipes leading to the second-stage reactor (56,59).

The acrolein-rich gaseous mixture containing some acrylic acid is then passed to the second-stage reactor, which is similar to the first-stage reactor, but packed with a catalyst designed for selective conversion of acrolein to acrylic acid. Here, the temperature peaks in the range of 280–360°C, again depending on conditions. The temperature of the effluent from the second-stage reactor again approximates that of the salt coolant. The heat of reaction is recovered as steam in external waste-heat boilers.

The process is operated at the lowest temperature consistent with high conversion. Conversion increases with temperature; the selectivity generally decreases only with large increases in temperature. Catalyst life also decreases with increasing temperatures. Catalysts are designed to give high performance over a range of operating conditions permitting gradual increase of salt temperature over the operating life of the catalysts to maintain productivity and selectivity near the initial levels, thus compensating for gradual loss of catalyst activity.

The gaseous reactor effluent from the second-stage oxidation is fed to the bottom of the aqueous absorber and cooled from about 250°C to less than 80°C by contact with aqueous acrylic acid. The gas passes through the absorber to complete the recovery of product. The water is fed to the top of the absorber at about 30–60°C to minimize acrylic acid losses and the absorber off-gas is sent to a flare or to a furnace to convert all residual organic material to waste gas. Some of the absorber off-gas may be recycled to the first-stage reactor feed to allow achievement of optimum oxygen-to-propylene ratio at reduced steam levels (59). If the resulting oxygen level is too low for best performance in the second-stage oxidation, an interstage feed of supplemental air (or air plus steam) may be introduced (56). The aqueous effluent from the bottom of the absorber is 30–60% acrylic acid depending on whether off-gas recycle with low steam feed or air feed with higher steam level is chosen. This is sent to the separations section for recovery. The overall yield of acrylic acid in the oxidation reaction steps is in the range of 75–86%, depending on the catalysts, conditions, and age of catalyst employed.

Acrylic Acid Recovery. The process flow sheet (Fig. 3) shows equipment and conditions for the separations step. The acrylic acid is extracted from the absorber effluent with a solvent, such as butyl acetate, xylene, diisobutyl ketone,

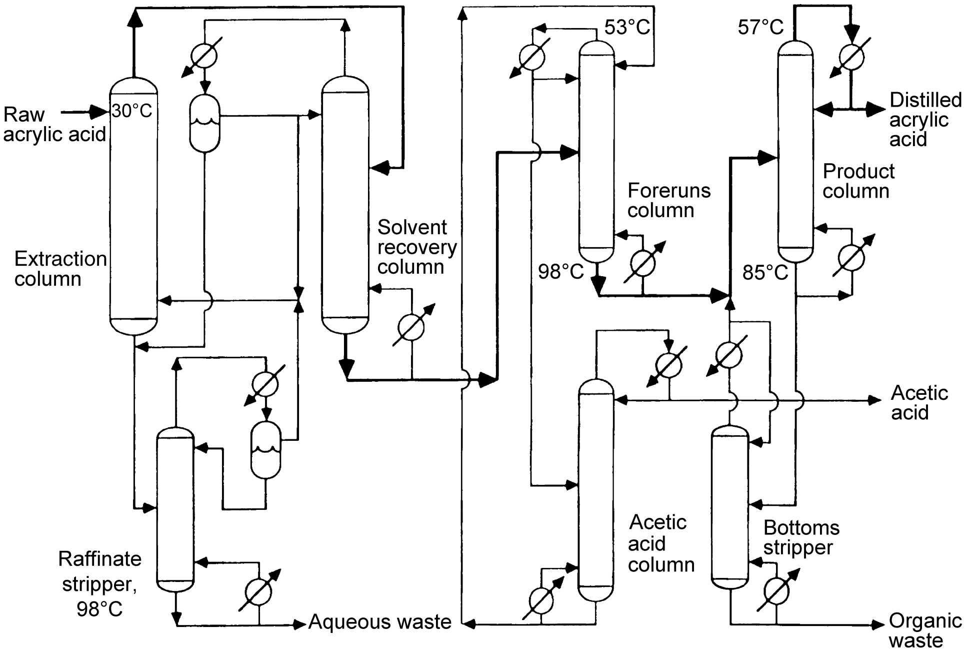


Fig. 3. Separations process.

or mixtures, chosen for high selectivity for acrylic acid and low solubility for water and by-products. The extraction is performed using 5–10 theoretical stages in a tower or centrifugal extractor (46,61–65).

The extract is vacuum-distilled in the solvent recovery column, which is operated at low bottom temperatures to minimize the formation of polymer and dimer and is designed to provide acrylic acid-free overheads for recycle as the extraction solvent. A small aqueous phase in the overheads is mixed with the raffinate from the extraction step. This aqueous material is stripped before disposal both to recover extraction solvent values and minimize waste organic disposal loads.

It is possible to dispense with the extraction step if the oxidation section is operated at high propylene concentrations and low steam levels to give a concentrated absorber effluent. In this case, the solvent recovery column operates at total organic reflux to effect azeotropic dehydration of the concentrated aqueous acrylic acid. This results in a reduction of aqueous waste at the cost of somewhat higher energy usage.

The bottoms from the solvent recovery (or azeotropic dehydration column) are fed to the foreruns column where acetic acid, some acrylic acid, and final traces of water are removed overhead. The overhead mixture is sent to an acetic acid purification column where a technical grade of acetic acid suitable for ester manufacture is recovered as a by-product. The bottoms from the acetic acid recovery column are recycled to the reflux to the foreruns column. The bottoms from the foreruns column are fed to the product column where the glacial acrylic acid of commerce is taken overhead. Bottoms from the product column are stripped to recover acrylic acid values and the high boilers are burned. The principal losses of acrylic acid in this process are to the aqueous raffinate and to the aqueous layer from the dehydration column and to dimerization of acrylic acid to 3-acryloxypropionic acid. If necessary, the product column bottoms stripper may include provision for a short-contact-time cracker to crack this dimer back to acrylic acid (60).

In any case, mild conditions and short residence times to minimize dimer formation are maintained throughout the separations section. In addition, free-radical polymerization inhibitors are fed to each unit to prevent polymer formation and resulting equipment failure. The glacial acrylic acid produced at this stage of the process is typically better than 99.5% pure, with the principal contaminants being water and acetic acid at about 0.1–0.2 wt %, acetic acid at about 0.1 wt %, and acrylic acid dimer at 0.1–0.5 wt % depending on storage time after distillation. Propionic acid is present at 0.02–0.04 wt %. The monomethyl ether of hydroquinone is added as storage and shipping stabilizer at 0.02 wt % (200 ppm). Low concentrations of aldehydes, primarily furfuraldehyde, but including acetaldehyde, acrolein, and benzaldehyde, may be present in commercial glacial acrylic acid. These impurities may have an adverse effect in achievement of very high molecular weight polymers. Further distillation or chemical treatment prior to final distillation is employed to remove carbonyl impurities. Effective agents include hydrazine, amino acids, and alkyl or aryl amines (66–68).

Esterification. The process flow sheet (Fig. 4) outlines the process and equipment of the esterification step in the manufacture of the lower acrylic esters

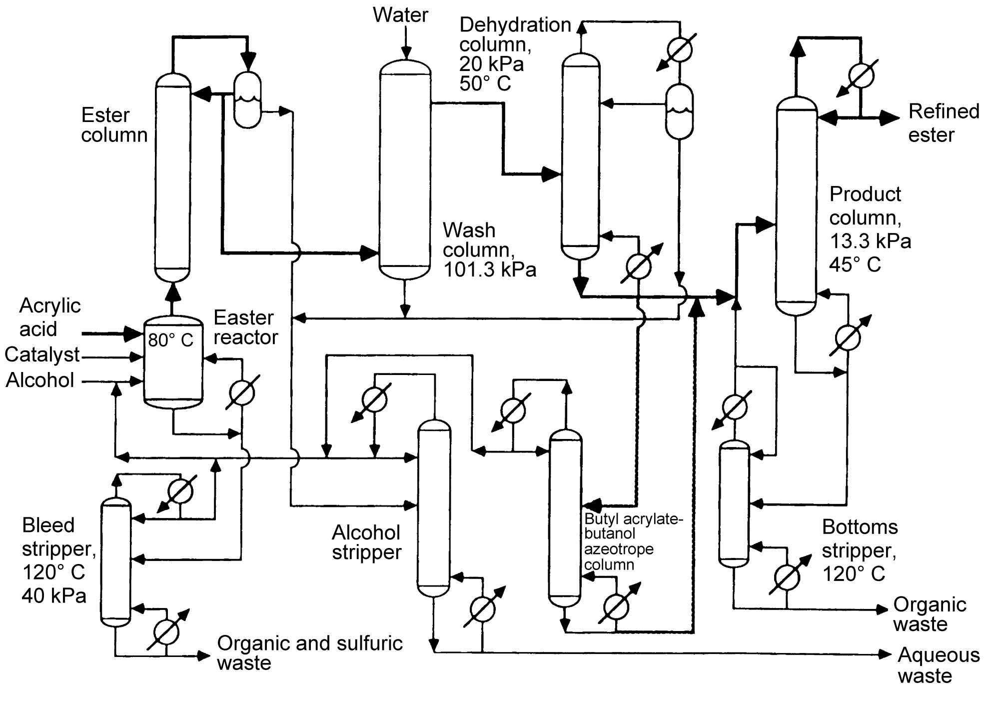


Fig. 4. Esterification process. To convert kPa to mm Hg, multiply by 7.5.

(methyl, ethyl, or butyl). For typical art, see References 69–74. The part of the flow sheet containing the dotted lines is appropriate only for butyl acrylate, since the lower alcohols, methanol and ethanol, are removed in the wash column. Since the butanol is not removed by a water or dilute caustic wash, it is removed in the azeotrope column as the butyl acrylate azeotrope; this material is recycled to the reactor.

Acrylic acid, alcohol, and the catalyst, eg, sulfuric acid, together with the recycle streams are fed to the glass-lined ester reactor fitted with an external reboiler and a distillation column. Acrylate ester, excess alcohol, and water of esterification are taken overhead from the distillation column. The process is operated to give only traces of acrylic acid in the distillate. The bulk of the organic distillate is sent to the wash column for removal of alcohol and acrylic acid; a portion is returned to the top of the distillation column. If required, some base may be added during the washing operation to remove traces of acrylic acid.

A continuous bleed is taken from the reactor to remove high boilers. Values contained in this bleed are recovered in the bleed stripper and the distillate from this operation is recycled to the esterification reactor. The bleed stripper residue is a mixture of high boiling organic material and sulfuric acid, which is recovered for recycle in a waste sulfuric acid plant.

If a waste sulfuric acid regeneration plant is not available, eg, as part of a joint acrylate–methacrylate manufacturing complex, the preferred catalyst for esterification is a sulfonic acid type ion-exchange resin. In this case the residue from the ester reactor bleed stripper can be disposed of by combustion to recover energy value as steam.

The wet ester is distilled in the dehydration column using high reflux to remove a water phase overhead. The dried bottoms are distilled in the product column to provide high purity acrylate. The bottoms from the product column are stripped to recover values and the final residue incinerated. Alternatively, the bottoms may be recycled to the ester reactor or to the bleed stripper.

Conventional polymerization inhibitors are fed to each of the distillation columns. The columns are operated under reduced pressure to give low bottom temperatures and minimize polymerization.

The aqueous layer from the ester column distillate, the raffinate from washing the ester, and the aqueous phase from the dehydration step are combined and distilled in the alcohol stripper. The wet alcohol distillate containing a low level of acrylate is recycled to the esterification reactor. The aqueous column bottoms are incinerated or sent to biological treatment. Biological treatment is common.

Process conditions for methyl acrylate are similar to those employed for ethyl acrylate. However, in the preparation of butyl acrylate the excess butanol is removed as the butanol–butyl acrylate azeotrope in the azeotrope column.

The esters are produced in minimum purity of 99.5%. The yield, based on acrylic acid, is in the range of about 95–98% depending on the ester and reaction conditions. Monomethyl ether of hydroquinone (10–100 ppm) is added as polymerization inhibitor and the esters are used in this form in most industrial polymerizations.

4.2. Acetylene-Based Routes. Walter Reppe, the father of modern acetylene chemistry, discovered the reaction of nickel carbonyl with acetylene and water or alcohols to give acrylic acid or esters (75,76). This discovery led to several processes which have been in commercial use. The original Reppe reaction requires a stoichiometric ratio of nickel carbonyl to acetylene. The Rohm and Haas modified or semicatalytic process provides 60–80% of the carbon monoxide from a separate carbon monoxide feed and the remainder from nickel carbonyl (77,78). The reactions for the synthesis of ethyl acrylate are

$$4\ C_2H_2 + 4\ C_2H_5OH + Ni(CO)_4 + 2\ HCl \longrightarrow 4\ CH_2{=}CHCOOC_2H_5 + H_2 + NiCl_2$$

$$C_2H_2 + C_2H_5OH + 0.05\ Ni(CO)_4 + 0.8\ CO + 0.1\ HCl \longrightarrow$$
$$CH_2{=}CHCOOC_2H_5 + 0.05\ NiCl_2 + 0.05\ H_2$$

The stoichiometric and the catalytic reactions occur simultaneously, but the catalytic reaction predominates. The process is started with stoichiometric amounts, but afterward, carbon monoxide, acetylene, and excess alcohol give most of the acrylate ester by the catalytic reaction. The nickel chloride is recovered and recycled to the nickel carbonyl synthesis step. The main by-product is ethyl propionate, which is difficult to separate from ethyl acrylate. However, by proper control of the feeds and reaction conditions, it is possible to keep the ethyl propionate content below 1%. Even so, this is significantly higher than the propionate content of the esters from the propylene oxidation route.

Other by-products formed are relatively easy to separate, including esters of higher unsaturated monobasic acids (alkyl 3-pentenoate and 3,5-heptadienoate) (5) and esters of multiply-unsaturated dibasic acids, eg, suberates.

The reaction is initiated with nickel carbonyl. The feeds are adjusted to give the bulk of the carbonyl from carbon monoxide. The reaction takes place continuously in an agitated reactor with a liquid recirculation loop. The reaction is run at about atmospheric pressure and at about 40°C with an acetylene:carbon monoxide mole ratio of 1.1:1 in the presence of 20% excess alcohol. The reactor effluent is washed with nickel chloride brine to remove excess alcohol and nickel salts and the brine–alcohol mixture is stripped to recover alcohol for recycle. The stripped brine is again used as extractant, but with a bleed stream returned to the nickel carbonyl conversion unit. The neutralized crude monomer is purified by a series of continuous, low pressure distillations.

The modified Reppe process was installed by Rohm and Haas at their Houston plant in 1948 and later expanded to a capacity of about 182×10^6 kg/yr. Rohm and Haas started up a propylene oxidation plant at the Houston site in late 1976. The combination of attractive economics and improved product purity from the propylene route led to a shutdown of the acetylene-based route within a year.

Reppe's work also resulted in the high pressure route which was established by BASF at Ludwigshafen in 1956. In this process, acetylene, carbon monoxide, water, and a nickel catalyst react at about 200°C and 13.9 MPa (2016 psi) to give acrylic acid. Safety problems caused by handling of acetylene are alleviated by the use of tetrahydrofuran as an inert solvent. In this process, the catalyst is a mixture of nickel bromide with a cupric bromide promotor. The liquid reactor effluent is degassed and extracted. The acrylic acid is obtained by distillation of the extract and subsequently esterified to the desired acrylic ester. The

BASF process gives acrylic acid, whereas the Rohm and Haas process provides the esters directly.

Nickel carbonyl is volatile, has little odor, and is extremely toxic. Symptoms of dangerous exposure may not appear for several days. Effective medical treatment should be started immediately. The plant should be designed to ensure containment of nickel carbonyl and to prevent operator contact.

All other organic waste-process and vent streams are burned in a flare, in an incinerator, or in a furnace where fuel value is recovered. Wastewater streams are handled in the plant biological treatment area.

A method for producing acrylic acid by acrolein oxidation using a metallic catalyst (M_0, W, V) has been described (79). The catalyst is broken into smaller pieces and suspended in water. This helps to prevent deterioration of the catalyst.

Although some very minor manufacturers of acrylic acid may still use hydrolysis of acrylonitrile (see below), essentially all other plants worldwide use the propylene oxidation process.

4.3. Acrylonitrile Route. This process, based on the hydrolysis of acrylonitrile (80), is also a propylene route since acrylonitrile (qv) is produced by the catalytic vapor-phase ammoxidation of propylene.

$$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}\,O_2 \longrightarrow CH_2{=}CHCN + 3\,H_2O$$

The yield of acrylonitrile based on propylene is generally lower than the yield of acrylic acid based on the direct oxidation of propylene. Hence, for the large volume manufacture of acrylates, the acrylonitrile route is not attractive since additional processing steps are involved and the ultimate yield of acrylate based on propylene is much lower. Hydrolysis of acrylonitrile can be controlled to provide acrylamide rather than acrylic acid, but acrylic acid is a by-product in such a process (81).

The sulfuric acid hydrolysis may be performed as a batch or continuous operation. Acrylonitrile is converted to acrylamide sulfate by treatment with a small excess of 85% sulfuric acid at 80–100°C. A hold-time of about 1 h provides complete conversion of the acrylonitrile. The reaction mixture may be hydrolyzed and the aqueous acrylic acid recovered by extraction and purified as described under the propylene oxidation process prior to esterification. Alternatively, after reaction with excess alcohol, a mixture of acrylic ester and alcohol is distilled and excess alcohol is recovered by aqueous extractive distillation. The ester in both cases is purified by distillation.

Important side reactions are the formation of ether and addition of alcohol to the acrylate to give 3-alkoxypropionates. In addition to high raw material costs, this route is unattractive because of large amounts of sulfuric acid–ammonium sulfate wastes.

4.4. Ketene Process. The ketene process based on acetic acid or acetone as the raw material was developed by B. F. Goodrich (82) and Celanese (83). It is no longer used commercially because the intermediate β-propiolactone is suspected to be a carcinogen (84). In addition, it cannot compete with the improved propylene oxidation process (see KETENES, KETENE DIMERS, AND RELATED SUBSTANCES).

4.5. Ethylene Cyanohydrin Process.

This process, the first for the manufacture of acrylic acid and esters, has been replaced by more economical ones. During World War I, the need for ethylene as an important raw material for the synthesis of aliphatic chemicals led to development of this process (16) in both Germany, in 1927, and the United States, in 1931.

In the early versions, ethylene cyanohydrin was obtained from ethylene chlorohydrin and sodium cyanide. In later versions, ethylene oxide (from the direct catalytic oxidation of ethylene) reacted with hydrogen cyanide in the presence of a base catalyst to give ethylene cyanohydrin. This was hydrolyzed and converted to acrylic acid and by-product ammonium acid sulfate by treatment with about 85% sulfuric acid.

Losses by polymer formation kept the yield of acrylic acid to 60–70%. Preferably, esters were prepared directly by a simultaneous dehydration–esterification process.

The process has historic interest. It was replaced at the Rohm and Haas Company by the acetylene-based process in 1954, and in 1970 at Union Carbide by the propylene oxidation process.

4.6. Other Syntheses.

Acrylic acid and other unsaturated compounds can also be made by a number of classical elimination reactions. Acrylates have been obtained from the thermal dehydration of hydracrylic acid (3-hydroxypropanoic acid [503-66-2]) (85), from the dehydrohalogenation of 3-halopropionic acid derivatives (86), and from the reduction of dihalopropionates (2). These studies, together with the related characterization and chemical investigations, contributed significantly to the development of commercial organic chemistry. Metallic oxide catalysts can produce acrylic acid by vapor phase catalytic oxidation of propane in high yield (87).

Vapor-Phase Condensations of Acetic Acid or Esters with Formaldehyde. Addition of a methylol group to the α-carbon of acetic acid or esters, followed by dehydration, gives the acrylates.

$$\mathrm{CH_3COOH(R) + CH_2O \longrightarrow CH_2{=}CHCOOH(R) + H_2O}$$

The reaction is generally carried out at atmospheric pressure and at 350–400°C. A variety of catalysts, eg, bases and metal salts and oxides on silica or alumina–silicates, have been patented (88–93). Conversions are in the 30–70% range and selectivities in the 60–90% range, depending on the catalyst and the ratio of formaldehyde to acetate.

The procedure is technically feasible, but high recovery of unconverted raw materials is required for the route to be practical. Its development depends on the improvement of catalysts and separation methods and on the availability of low cost acetic acid and formaldehyde. Both raw materials are dependent on ample supply of low cost methanol.

Although the rapid cost increases and shortages of petroleum-based feedstocks forecast a decade ago have yet to materialize, shift to natural gas or coal may become necessary. Under such conditions, it is possible that acrylate manufacture via acetylene, as described above, could again become attractive.

It appears that condensation of formaldehyde with acetic acid might be preferred. A coal gasification complex readily provides all of the necessary intermediates for manufacture of acrylates (94).

Oxidative Carbonylation of Ethylene—Elimination of Alcohol from β-Alkoxypropionates. Spectacular progress in the 1970s led to the rapid development of organotransition-metal chemistry, particularly to catalyze olefin reactions (95,96). A number of patents have been issued (28,97–99) for the oxidative carbonylation of ethylene to provide acrylic acid and esters. The procedure is based on the palladium catalyzed carbonylation of ethylene in the liquid phase at temperatures of 50–200°C. Esters are formed when alcohols are included. Anhydrous conditions are desirable to minimize the formation of by-products including acetaldehyde and carbon dioxide (see ACETALDEHYDE).

During the reaction, the palladium catalyst is reduced. It is reoxidized by a co-catalyst system such as cupric chloride and oxygen. The products are acrylic acid in a carboxylic acid-anhydride mixture or acrylic esters in an alcoholic solvent. Reaction products also include significant amounts of 3-acryloxypropionic acid [24615-84-7] and alkyl 3-alkoxypropionates, which can be converted thermally to the corresponding acrylates (23,100). The overall reaction may be represented by:

$$\mathrm{CH_2{=}CH_2 + CO + HOR + \frac{1}{2}\,O_2 \longrightarrow CH_2{=}CHCOOR + H_2O}$$

It is preferrable to carry out the reactions to give an intermediate β-alkoxypropionate. When the reaction is carried out in ethanolic ethyl β-ethoxypropionate as solvent, and a trace of mercury(II) is included in the catalyst system, the yield of intermediate ethyl β-ethoxypropionate rises to 95–97%; the principal by-product is the corresponding β-chloropropionate ester. Acid-catalyzed thermal cracking of the mixture at 120–150°C gives very high yields of ethyl acrylate (26). Although yields are excellent, the reaction medium is extremely corrosive, so high cost materials of construction are necessary. In addition, the high cost of catalyst and potential toxicity of mercury require that the inorganic materials be recovered quantitatively from any waste stream. Hence, high capital investment, together with continued favorable costs for propylene, have prevented commercialization of this route.

The elimination of alcohol from β-alkoxypropionates can also be carried out by passing the alkyl β-alkoxypropionate at 200–400°C over metal phosphates, silicates, metal oxide catalysts (101), or base-treated zeolites (98). In addition to the route via oxidative carbonylation of ethylene, alkyl β-alkoxypropionates can be prepared by reaction of dialkoxy methane and ketene (102).

Dehydrogenation of Propionates. Oxidative dehydrogenation of propionates to acrylates employing vapor-phase reactions at high temperatures (400–700°C) and short contact times is possible. Although selective catalysts for the oxidative dehydrogenation of isobutyric acid to methacrylic acid have been developed in recent years (see METHACRYLIC ACID AND DERIVATIVES) and a route to methacrylic acid from propylene to isobutyric acid is under pilot-plant development in Europe, this route to acrylates is not presently of commercial interest because of the combination of low selectivity, high raw material costs, and purification difficulties.

Liquid-Phase Oxidation of Acrolein. As discussed before, the most attractive process for the manufacture of acrylates is based on the two-stage, vapor-phase oxidation of propylene. The second stage involves the oxidation of acrolein. Considerable art on the liquid-phase oxidation of acrolein (17) is available, but this route cannot compete with the vapor-phase technology.

5. Specialty Acrylic Esters

Higher alkyl acrylates and alkyl-functional esters are important in copolymer products, in conventional emulsion applications for coatings and adhesives, and as reactants in radiation-cured coatings and inks. In general, they are produced in direct or transesterification batch processes (17,103,104) because of their relatively low volume.

Direct, acid catalyzed esterification of acrylic acid is the main route for the manufacture of higher alkyl esters. The most important higher alkyl acrylate is 2-ethylhexyl acrylate prepared from the available oxo alcohol 2-ethyl-1-hexanol (see ALCOHOLS, HIGHER ALIPHATIC). The most common catalysts are sulfuric or toluenesulfonic acid and sulfonic acid functional cation-exchange resins. Solvents are used as entraining agents for the removal of water of reaction. The product is washed with base to remove unreacted acrylic acid and catalyst and then purified by distillation. The esters are obtained in 80–90% yield and in excellent purity.

Transesterification of a lower acrylate ester and a higher alcohol (104,105) can be performed using a variety of catalysts and conditions chosen to provide acceptable reaction rates and to minimize by-product formation and polymerization.

$$\mathrm{CH_2{=}CHCOOR + R'OH \xrightarrow{H^+} CH_2{=}CHCOOR' + ROH}$$

Pure dry reactants are needed to prevent catalyst deactivation; effective inhibitor systems are also desirable as well as high reaction rates, since many of the specialty monomers are less stable than the lower alkyl acrylates. The alcohol–ester azeotrope (8) should be removed rapidly from the reaction mixture and an efficient column used to minimize reactant loss to the distillate. After the reaction is completed, the catalyst may be removed and the mixture distilled to obtain the ester. The method is particularly useful for the preparation of functional monomers which cannot be prepared by direct esterification. Dialkylaminoethyl acrylic esters are readily prepared by transesterification of the corresponding dialkylaminoethanol (104,105). Catalysts include strong acids and tetraalkyl titanates for higher alkyl esters; and titanates, sodium phenoxides, magnesium alkoxides, and dialkyltin oxides, as well as titanium and zirconium chelates, for the preparation of functional esters. Because of loss of catalyst activity during the reaction, incremental or continuous additions may be required to maintain an adequate reaction rate.

Table 5. **Acrylic Acid Producers and Capacities, U.S., $\times 10^6$ kg ($\times 10^6$ lb)**

Producer	Capacity
BASF, Freeport, Tex.	220 (485)
American Acryl, Pasadena, Tex.	120 (265)
Celanese, Clear Lake, Tex.	290 (640)
Dow Chemical, Taft, La.	109 (240)
Rohm and Haas/StoHaas, Deer Park, Tex.	573 (1265)
Total	*1312 (2895)*

Hydroxyethyl and 2-hydroxypropyl acrylates are prepared by the addition of ethylene oxide or propylene oxide to acrylic acid (106,107).

The reactions are catalyzed by tertiary amines, quaternary ammonium salts, metal salts, and basic ion-exchange resins. The products are difficult to purify and generally contain low concentrations of acrylic acid and some diester which should be kept to a minimum since its presence leads to product instability and to polymer cross-linking.

6. Economic Aspects

Table 5 lists United States producers of acrylic acid and their capacities. Industrial production is by gas-phase oxidation of propylene. About three quarters of the production is converted directly into acrylate esters and the rest is purified into glacial acrylic acid (108).

Rohm and Haas formed a fifty-fifty joint venture with Stockhausen (Krefeld, Germany). The new company, StoHaas (Marl, Germany) has expanded capacity to 34×10^6 kg (75×10^6 lb) at Deer Park, Texas and plans to produce 100×10^6 kg (220×10^6 lb) in Marl in 2003. Acrylic acid and esters are marketed exclusively by Rohm and Haas.

Growth for acrylic acid is estimated at 4.0% per year and should reach 1.8×10^9 kg (2.6×10^9 lb) in 2004. *n*-Butyl acrylate is the most important of the esters and demand will grow at the rate of 4.2% (108).

Prices for the period 1995–2001 ranged from \$0.37 to \$0.39/kg (\$0.81-0.87/lb), list, glacial acrylic acid, tanks, dil. Current prices: \$0.39/kg (\$0.87/lb), same basis. Market price: \$0.28 to \$0.32/kg (\$0.62–0.70/lb) same basis (108).

7. Analytical Methods

Chemical assay is preferably performed by gas–liquid chromatography (glc) or by the conventional methods for determination of unsaturation such as bromination or addition of mercaptan, sodium bisulfite, or mercuric acetate.

Acidity is determined by glc or titration, and the dimer content of acrylic acid by glc or a saponification procedure. The total acidity is corrected for the dimer acid content to give the value for acrylic acid.

The relatively low flash points of some acrylates create a fire hazard. Also, the ease of polymerization must be borne in mind in all operations. The lower and upper explosive limits for methyl acrylate are 2.8 and 25 vol %, respectively. Corresponding limits for ethyl acrylate are 1.8 vol % and saturation, respectively. All possible sources of ignition of monomers must be eliminated.

8. Storage and Handling

Acrylic acid and esters are stabilized with minimum amounts of inhibitors consistent with stability and safety. The acrylic monomers must be stable and there should be no polymer formation for prolonged periods with normal storage and shipping (4,109). The monomethyl ether of hydroquinone (MEHQ) is frequently used as inhibitor and low inhibitor grades of the acrylate monomers are available for bulk handling. MEHQ at 10–15 ppm is generally adequate for the esters, but a higher concentration (200 ppm) is needed for acrylic acid.

The effectiveness of phenolic inhibitors is dependent on the presence of oxygen and the monomers must be stored under air rather than an inert atmosphere. Temperatures must be kept low to minimize formation of peroxides and other products. Moisture may cause rust-initiated polymerization.

Acrylic acid has a relatively high freezing point (13°C) and the inhibitor may not be distributed uniformly between phases when frozen acid is partially thawed. If the liquid phase is inadequately inhibited, it could polymerize and initiate violent polymerization of the entire mass. Provisions should be made to maintain the acid as a liquid. High temperatures should be avoided because of dimer formation. If freezing should occur, melting should take place at room temperature (25°C); material should not be withdrawn until the total is thawed and well-mixed to provide good distribution of the inhibitor and dissolved oxygen. No part of the mass should be subjected to elevated temperatures during the melting process.

Dimer formation, which is favored by increasing temperature, generally does not reduce the quality of acrylic acid for most applications. The term dimer includes higher oligomers formed by further addition reactions and present in low concentrations relative to the amount of dimer (3-acryloxypropionic acid). Glacial acrylic acid should be stored at 16–29°C to maintain high quality.

The acrylic esters may be stored in mild or stainless steel, or aluminum. However, acrylic acid is corrosive to many metals and can be stored only in glass, stainless steel, aluminum, or polyethylene-lined equipment. Stainless steel types 316 and 304 are preferred materials for acrylic acid.

For most applications, the phenolic inhibitors do not have to be removed. The low-inhibitor grades of acrylic monomers are particularly suitable for the manufacture of polymer without pretreatment. Removal of inhibitor from ester is best done by adsorption with ion-exchange resins or other adsorbents. Phenolic inhibitors may be removed from esters with an alkaline brine wash, generally a solution containing 5% caustic and 20% salt. Vigorous agitation during washing should be avoided to prevent the formation of emulsions. The washed monomers may be used without drying in emulsion processes. Washed uninhibited monomers are less stable and should be used promptly. They should be stored under refrigeration, but should not be permitted to freeze because of the danger of explosive polymerization during thawing. The heat of polymerization is approximately 75 kJ/mol (18 kcal/mol).

A method for transporting and storing pure acrylic acid comprises ensuring means of appropriate measures that the acrylic acid is partly crystalline during the entire duration of transport or storage (110).

9. Health and Safety Factors

The toxicity of common acrylic monomers has been characterized in animal studies using a variety of exposure routes. Toxicity varies with level, frequency, duration, and route of exposure. The simple higher esters of acrylic acid are usually less absorbed and less toxic than lower esters. In general, acrylates are more toxic than methacrylates. Data appear in Table 6.

With respect to acute toxicity, based on lethality in rats or rabbits, acrylic monomers are slightly to moderately toxic. Mucous membranes of the eyes, nose, throat, and gastrointestinal tract are particularly sensitive to irritation. Acrylates can produce a range of eye and skin irritations from slight to corrosive depending on the monomer.

Full eye protection should be worn whenever handling acrylic monomers; contact lenses must never be worn. Prolonged exposure to liquid or vapor can result in permanent eye damage or blindness. Excessive exposure to vapors causes nose and throat irritation, headaches, nausea, vomiting, and dizziness or drowsiness (solvent narcosis). Overexposure may cause central nervous system depression. Both proper respiratory protection and good ventilation are necessary wherever the possibility of high vapor concentration arises.

Table 6. **Acute Toxicity of Acrylic Acid and Esters**

Monomer	Methyl acrylate	Ethyl acrylate	Butyl acrylate	Acrylic acid
rat oral LD$_{50}$, g/kg	0.3	0.8–1.8	3.7–8.1	0.3–2.5
rabbit dermal LD$_{50}$, g/kg	1.3	1.2–3.0	1.7–5.7	0.3–1.6
rat inhalation LC$_{50}$, ppm	750–1350	2180	2370	1200–4000
rabbit eye irritation	severe to corrosive	severe to corrosive	slight to moderate	corrosive
rabbit skin irritator	severe irritation	severe irritation	moderate	corrosive
odor threshold, ppb	2.3–4.8	0.5	35^{a}	94^{b}
TLV/TWA^{c,d}, mg/m^{3}	35	20	52	5.9
ppm	10, skin	5	10	2, skin
STEL^{d}, mg/m^{3}		100		
ppm		25		
		A–2 suspect human carcinogen		

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[a] May have delayed eye irritation.

[b] Vapor exposure can cause irreversible eye damage.

[c] Ref. 107.

[d] Ref. 83.

Swallowing acrylic monomers may produce severe irritation of the mouth, throat, esophagus, and stomach, and cause discomfort, vomiting, diarrhea, dizziness, and possible collapse.

Skin redness and from slight to corrosive irritation is caused by direct contact. Acrylic acid is more corrosive than esters. The monomers not only irritate the skin, but may also be absorbed through the skin. Therefore, gloves and protective clothing and shoes or boots should be used in addition to eye (or full face) protective equipment. Upon contact, the skin should be flushed with copious amounts of water; follow-up medical attention should be sought. Medical attention should also be obtained if any of the earlier mentioned symptoms appear.

Repeated exposures to acrylic monomers can produce allergic dermatitis (or skin sensitization) resulting in rash, itching, or swelling. After exposure to one monomer, this dermatitis may arise upon subsequent exposure to the same or even a different acrylic monomer.

Repeated exposures of animals to high (near-lethal) concentrations of vapors result in inflammation of the respiratory tract, as well as degenerative changes in the liver, kidneys, and heart muscle. These effects arise at concentrations far above those causing irritation. Such effects have not been reported in humans. The low odor threshold and irritating properties of acrylates cause humans to leave a contaminated area rather than tolerate the irritation.

Current TLV/TWA values are provided in *Material Safety Data Sheets* provided by manufacturers upon request. Values (83,111,112) appear in Table 5.

Acrolein, acrylamide, hydroxyalkyl acrylates, and other functional derivatives can be more hazardous from a health standpoint than acrylic acid and its simple alkyl esters. Furthermore, some derivatives, such as the alkyl 2-chloroacrylates, are powerful vesicants and can cause serious eye injuries. Thus, although the hazards of acrylic acid and the normal alkyl acrylates are moderate and they can be handled safely with ordinary care to industrial hygiene, this should not be assumed to be the case for compounds with chemically different functional groups (see INDUSTRIAL HYGIENE; PLANT SAFETY; TOXICOLOGY).

In 1983 the National Toxicology Program (NTP) reported that ethyl acrylate produced tumors in the rodent forestomach after gavage (forced feeding via stomach tube) for 2 yr. The response occurred only at the site of contact after lifetime exposure to levels that were both irritating and ulcerating to that tissue. Based on this study, both the NTP and the International Agency for Research on Cancer (IARC) concluded that there was sufficient evidence for carcinogenicity of ethyl acrylate in experimental animals and by extension classified ethyl acrylate as possibly carcinogenic in humans. Several other studies of simple acrylate esters using alternate exposure methods failed to show evidence of oncogenic response.

9.1. Regulation. Acrylic acid and certain esters may be used safely as a component of the uncoated or coated food-product surface of paper and paperboard intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting and holding of dry food (21 CFR 176.180).

Acrylic acid polymers may be used as indirect food additives only for components of adhesives (21 CFR 175.105). Semirigid and rigid acrylic and modified acrylic plastics may be safely used as articles intended for use in contact with food and as components of articles intended for use in contact with food (21 CFR 177.1010).

10. Uses

Most acrylic acid is consumed in the form of the polymer. The dominant share of acrylic acid is converted to esters. Today growth is in the demand for superabsorbents (SAPs) for use in diapers and hygienic products. Acrylic acid accounts for 80–85% of raw materials used in the manufacture of SAPs.

Poly(acrylic acid) and salts (includes superabsorbent polymers, detergents, water treatment, and dispersants) account for 34% of total consumption; *n*-butyl acrylate, 32%; ethyl acrylate, 18%; 2-ethyl hexyl acrylate, 6%; methyl and specialty acrylates, 7%; and miscellaneous uses, 3% (108).

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