Kirk-Othmer Encyclopedia of Chemical Technology.
Copyright © John Wiley & Sons, Inc. All rights reserved.

CARBOXYLIC ACIDS, ECONOMIC ASPECTS

Aliphatic carboxylic acids produced on a reasonably significant commercial scale range from acetic acid (two carbons or C2) through stearic acid (C18). Lesser amounts of commercially available shorter chain-length acids, such as formic (C1), and longer chain-length acids, such as erucic (unsaturated C22) and behenic (saturated C22), are also produced. As a general rule, all of the even chain-length, nonisomeric acids from C6 to C22 are produced from naturally occurring fats and oils. A significant proportion of the lower chain-length (C1–C6) and longer isomeric chain-length (C7–C10) acids are made synthetically.

1. Nonoleo-Based Carboxylic Acids

Some of the more prominent carboxylic acids that are not fat- or oil-based include acetic, acrylic, and olefin-based propionic, butyric/isobutyric, 2-ethylhexanoic, heptanoic, pelargonic, neopentanoic, and neodecanoic. Table 1 summarizes the production, pricing, and primary producers of these acids.

With the exception of acetic, acrylic, and benzoic all other acids in Table 1 are primarily produced using oxo chemistry (see Oxo process). Propionic acid is made by the liquid-phase oxidation of propionaldehyde, which in turn is made by application of the oxo synthesis to ethylene. Propionic acid can also be made by oxidation of propane or by hydrocarboxylation of ethylene with CO and H_2 in the presence of a rhodium (2) or iridium (3) catalyst. Butyric acid is made by air-oxidation of butyraldehyde, which is obtained by application of the oxo synthesis to propylene. Isobutyric acid is made from isobutyraldehyde, a significant product in the synthesis of butyraldehyde (see Butyraldehydes). Butyraldehyde is also used to make 2-ethylhexanoic acid.

Rhodium catalyst is used to convert linear alpha-olefins to heptanoic and pelargonic acids (see Carboxylic acids, manufacture). These acids can also be made from the ozonolysis of oleic acid, as done by the Henkel Corp. Emery Group, or by steam cracking methyl ricinoleate, a by-product of the manufacture of nylon-11, an Atochem process in France (4). Neoacids are derived from isobutylene and nonene (4) (see Carboxylic acids, trialkylacetic acids).

Acetic acid (qv) can be produced synthetically (methanol carbonylation, acetaldehyde oxidation, butane/naphtha oxidation) or from natural sources (5). Oxygen is added to propylene to make acrolein, which is further oxidized to acrylic acid (see Acrylic acid and derivatives). An alternative method adds carbon monoxide and/or water to acetylene (6). Benzoic acid (qv) is made by oxidizing toluene in the presence of a cobalt catalyst (7).

2. Oleo-Based Carboxylic Acids

Worldwide capacity for production of higher aliphatic carboxylic acids (predominantly C8–C18), commonly called fatty acids, is about 3.5 million metric tons, with an additional 400,000 metric tons because of start-up over the next 1–2 years, mostly in southeast Asia. Worldwide production of these higher (and linear) fatty acids

Table 1. 1988–1991 U.S. Statistics on Non-Fat and Oil-Based Acids[a]

Acid	Production, 10^3 t	Price, $/kg	Producers	Applications
acetic (C2)	1538	0.62–0.68	Borden, Eastman, Hoechst Celanese, Quantum, Sterling, Union Carbide	vinyl acetate; acetic anhydride; acetate esters; TPA/DMT plastics
acrylic (C3)	490	1.45	BASF, Hoechst Celanese, Rohm & Haas, Union Carbide	acrylate esters (latex coatings, adhesives, polishes, etc)
propionic (C3)	54	0.73–0.82	Eastman, Hoechst Celanese, Union Carbide	grain and feed preservative; propionate salts; pesticides; cellulose acetate
butyric/isobutyric (C4)	24		Eastman, Hoechst Celanese	cellulose acetate butyrate (plastic); pesticides (isobutyric)
2-ethylhexanoic (C8)	12	1.25	Eastman, Union Carbide	paint driers; heat stabilizers for PVC
benzoic (C7)	43	1.21–3.86	Kalama, Pfizer, Velsicol	benzoate plasticizers; benzoate salts (preservative)
heptanoic/pelargonic (C7/C9)	20	1.40–1.80	Hoechst Celanese	polyol esters for synthetic lubricants; tetraethylene glycol diheptanoate plasticizer
neoacids (C5–C10)	18	1.30–2.15	Exxon	peroxy esters (polymerization initiators); pivaloyl chloride (polymerization, pharmaceuticals)

[a] Ref. 1

Table 2. Typical Composition of Specific Fats and Oils, %

Acid (chain length)	Lauric oils: Coconut	Lauric oils: Palm kernel	Tallow[a]	Palm stearine	Soybean	Tall Oil[b]	High erucic rapeseed[c]
Saturated acids							
caproic (C6)							
caprylic (C8)	7	3					
capric (C10)	6	3					
lauric (C12)	50	50			0.5		
myristic (C14)	18	18	3		0.5		
palmitic (C16)	8.5	8	24	51	12		3
stearic (C18)	3	2	20	5	4	2	1
Unsaturated acids[d]							
palmitoleic (C16:1)			2.5				
oleic (C18:1)	6	14	43	33	25	59	18
linoleic (C18:2)	1	2	4	9	52	37	14
linolenic (C18:3)	0.5		0.5		6		7
arachidonic (C20:1)						1	10
erucic (C22:1)							46

[a] Also contains ∼1% of myristoleic acid (C14:1)[d].
[b] Also contains ∼1% of arachidic acid (C20).
[c] Also contains ∼0.5% each of arachidic and behenic acid (C22).
[d] The number following the colon indicates the number of sites of unsaturation.

Table 3. Saturated Fatty Acid Production and Disposition[a], 10^3 t

Fatty acid	1985	1990
Production		
whole coconut oil-type acids[b,c]		
IV under 5	28.5	49.7
IV 5 or more	8.9	
fractionated and/or stripped acids		
C14 and lower	22.4	30.6
C16 and C18	31.3	26.1
stearic acid		
C18 content under 75%	204.3	227.1
C18 content 75% or more	10.4	16.3
Total saturated fatty acids	*305.8*	*349.8*
Disposition		
domestic shipments	231.0	264.2
captive consumption	54.1	77.9
export shipments	4.6	
Total	*289.7*	*342.1*

[a] Ref. 10.
[b] Includes palm kernel and babassu.
[c] IV = Iodine value.

Table 4. Unsaturated Fatty Acid Production and Disposition[a], 10^3 t

Fatty acid	1985	1990
Production		
oleic acid	79.8	85.9
unsaturated fatty acids other than oleic[b,c]		
IV 36 to under 80	60.6	46.0
IV 80 to under 130	7.1	17.5
IV 130 or more	7.5	
Total unsaturated fatty acids	*155.1*	*149.4*
Disposition		
domestic shipments	92.6	155.1
captive consumption	60.8	
export shipments	2.4	
Total	*155.9*	*155.1*

[a] Ref. 10.
[b] Includes tallow and palm acids.
[c] IV = Iodine value.

in 1988 was estimated at 2.6 million metric tons, with annual growth estimated at 2–3% (8). U.S. production of these C8–C18 linear acids, including tall oil (9), was reported to be approximately 660,000 metric tons, a figure that would appear to be understated. The use of these fatty acids covers many consumer product and industrial applications and historically has correlated well with the GNP in the United States.

Typically, fatty acids make up between 87 and 90% of the fat or oil from which they are made; the remaining 10–13% is glycerol. The most often used raw materials are coconut or palm kernel oil (lauric oils) for C8, C10, C12, and C14 acids; tallow, lard, and palm stearine for C16 and C18 acids; and soybean, sunflower, canola, and tall oil for whole cut unsaturated (lower melting point) acids. Fully hardened soya, canola, or edible tallow are usually used when high C18 food-grade stearic acid is needed, whereas edible tallow and tall oil are the primary raw materials for food-grade oleic. C22 acid is derived from rapeseed and/or marine oil

Table 5. Total[a] Production and Disposition of All Fatty Acids, 10^3 t[b]

	1985	1990
production	460.9	499.3
disposition		
domestic shipments	323.7	419.3
captive consumption	114.9	77.9
export shipments	7.1	
Total disposition	*445.6*	*497.2*

[a] Sum of Tables 3 and 4.
[b] Ref. 10.

(menhaden). Tall oil, a by-product of the kraft pulp and paper industry, is not a triglyceride and therefore does not contain glycerol (see Carboxylic acids, fatty acids from tall oil). Castor oil (qv) is the primary source for ricinoleic acid or 12-hydroxystearic acid when hardened. The compositions of some of these fats and oils are outlined in Table 2 (see also Table 1 of Carboxylic acids, manufacture).

With the exception of tall oil and castor oil acids, and acids used for sodium and potassium soaps, Tables 3, 4, and 5 provide detailed production and disposition information on the U.S. triglyceride-based fatty acids. These data show a 2–3%/yr growth rate between 1985 and 1990, virtually in line with world projections, with the most significant growth occurring in the stearic and coconut acid segments.

Fatty acids are produced by hydrolysis (splitting), during which the triglyceride (fat or oil) reacts with water, under high temperature and pressure, to yield glycerol and free fatty acids. Historically, hydrolysis was carried out in the presence of a catalyst, but today most U.S. producers make fatty acids in a noncatalytic system. At this point in the process the fatty acids resemble the chain-length distribution of the fat or oil feedstock, and simply undergo distillation to remove color and odor impurities to make a whole cut fatty acid ready for sale. Split and distilled acids that do not undergo any further processing comprise about 10% of the U.S. market as defined by the SDA statistics in Tables 3, 4, and 5.

The majority of whole cut fatty acids are further processed for additional differentiation. Adding hydrogen (hydrogenation) removes double bonds and therefore increases stability and hardness. Acids can be either partially or fully hydrogenated depending on the properties needed, ie, melting point, reactivity, etc, for a particular application. Partially hardened (intermediate melting point) and fully hardened (high melting point) whole cut acids amount to about 45% of U.S. acid production.

Unhardened whole cut tallow and palm acids contain 40–45% oleic acid, which is derived by separation technology. This used to be done by a pressing technique; thereby the terminology *pressed* stearics. In the 1990s the separation is done using solvents and/or refrigeration techniques. Oleic and pressed stearics account for about one-third of all U.S. acid production.

Whole cut acids can also undergo fractional distillation to produce fractionated acids with a high percentage content of a specific chain length, eg, 99% lauric, 95% myristic, etc. The markets for these acids are generally more specialty in nature and thereby deliver higher realization than whole cut split distilled, hydrogenated, or separated acids. Fractionated acids fill the remaining 10–12% of U.S. market demand.

Table 6 provides information on average 1991 pricing for various fatty acids as well as listing U.S. producers and typical applications for each type of acid. The U.S. fatty acid industry experienced considerable consolidation in the 1980s, whereby there are 16 active producers today, down from about 25 in the 1970s. The number of sites producing fatty acids has undergone even more extensive consolidation as the trend has been toward larger, lower cost, more fully integrated facilities.

Because they are made from renewable natural raw materials, oleo-based fatty acids are completely biodegradable and find widespread usage in a variety of applications and industries, as is evident from Table 6.

Table 6. Oleo-Based Carboxylic Acids

Acid	Price[a],$/kg 1991	U.S. producers	Applications
		Oil specific acids	
canola	0.95	Henkel/Emery, Procter& Gamble, Sherex	surfactants
castor oil acids (ricinoleic, 12-hydroxystearic)	1.75	Caschem, Union Camp	lubricating greases
coconut oil acids	0.80–1.20	Dial, Henkel/Emery, Procter& Gamble, Witco, Karlshamns	surfactants, soap
hydrogenated and/or separatedtallow-based acids	0.65	Akzo, Henkel/Emery, Lonza, Procter & Gamble, Sherex, Synpro, Unichema, Witco	metallic stearates (plastic lubricants), tires, candles, crayons, cosmetics
soybean oil acids	0.90	Henkel/Emery, Procter & Gamble, Witco	alkyd resins (paint)
tall oil acids			
2% or more rosin	0.55	Arizona, Georgia-Pacific, Hercules,	alkyd resins, ore flotation
less than 2%	0.60	Union Camp, Westvaco	
tallow fatty acids	0.60	Akzo, Dial, Henkel/Emery, Lonza, Procter & Gamble, Sherex, Synpro. Unichema, Witco	soap, lubricants, fabric softeners, asphalt emulsifiers, synthetic rubber, plastics
Chain-length specific acids			
capric	2.05	Akzo, Henkel/Emery, Procter & Gamble, Witco	synthetic lubricants, medium-chain triglycerides
caprylic	1.85	Akzo, Henkel/Emery, Procter & Gamble, Witco	synthetic lubricants, medium-chain triglycerides
caprylic-capric blend	1.30	Akzo, Dial, Henkel/Emery, Procter & Gamble, Witco	synthetic lubricants, medium-chain triglycerides
lauric, 95% (dodecanoic)	1.30	Akzo, Henkel/Emergy, Procter & Gamble, Witco	surfactants, soap
myristic, 95% (tetradecanoic)	1.54	Henkel/Emergy, Procter & Gamble, Witco	esters for cosmetics, lotions
oleic	1.10	Henkel/Emery, Hercules, Unichema, Witco	surfactants, lubricants, plasticizers
palmitic, 90%	1.20	Henkel/Emery, Procter & Gamble, Sherex, Witco	esters for personal care products
pelargonic (nonanoic)	2.10	Henkel/Emery	synthetic lubricants, plasticizers
stearic, 90%	1.00	Akzo, Henkel/Emery, Lonza, Procter & Gamble, Sherex, Synpro, Unichema, Witco	alkyd resins, ore flotation

[a] Ref. 11.

Table 7 (12) summarizes the consumption of fatty acids by end use industry in 1987, supporting the broad base of usage and explaining the relationship with GNP.

Table 7. U.S. Consumption[ab] of Fatty Acids by Market Area in 1987, 10^3 t

household and industrial cleaners	124
coatings and adhesives (including paints and inks)	88
personal care products (excluding toilet soap)	86
industrial lubricants, corrosion inhibitors, and oil field applications	85
plastics (excluding emulsion polymerization)	81
household fabric softeners	50
rubber (excluding emulsion polymerization)	39
emulsion polymerization	29
textiles (including textile fabric softeners)	29
foods	19
asphalt	12
paper	11
mining	8
crayons, candles, and waxes	7
miscellaneous, unassigned, and exported derivatives (including nitriles)	69
Total	*737*

[a] Estimates are based on direct consumption of the acid or ultimate consumption of various derivatives.
[b] Ref. 12.

BIBLIOGRAPHY

"Fatty Acids (Economic Aspects)" in *ECT* 2nd ed., Vol. 8, pp. 839–845, by E. H. Pryde, U.S. Department of Agriculture; "Carboxylic Acids (Economic Aspects)" in *ECT* 3rd ed., Vol. 4, pp. 853–859, by E. H. Pryde, U.S. Department of Agriculture.

Cited Publications

1. *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1991.
2. U.S. Pat. 3,989,747 (Nov. 2, 1976), J. H. Craddock, J. F. Roth, A. Hershman, and F. E. Paulik (to Monsanto Co.).
3. U.S. Pat. 3,989,748 (Nov. 2, 1976), F. E. Paulik, A. Hershman, J. F. Roth, and J. H. Craddock (to Monsanto Co.).
4. T. Gibson and T. Sasano, "Oxo Chemicals," in *Chemical Economics Handbook Marketing Research Report*, SRI International, Menlo Park, Calif., Jan. 1991.
5. K. Wheeler, "Acetic Acid," in K. Wheeler, "Acetic Acid," *Chemical Economics Handbook Marketing Research Report*, SRI International, Menlo Park, Calif., Dec. 1988.
6. M. Fox, T. Gibson, R. Mulach, and T. Sasano, "Acrylic Acid and Esters," in *Chemical Economics Handbook Marketing Research Report*, SRI International, Menlo Park, Calif., Feb. 1990.
7. H. Chinn, "Benzoic Acid—U.S.," in H. Chinn, "Benzoic Acid—U.S.," *Chemical Economics Handbook Data Summary*, SRI International, Menlo Park, Calif., June 1989.
8. A. J. Kaufman and R. J. Ruebusch, *Oleochemicals: A World Overview*, presented at *World Conference on Oleochemicals—Into the 21st Century*, Kuala Lumpur, Malaysia, Henkel Corp., Emery Group, Oct. 1990; adjusted by author estimates for worldwide tall oil and castor acids.
9. M2OK Report, U.S. Bureau of the Census, Washington, D.C., 1990.
10. Glycerine and Oleochemical Division, The Soap and Detergent Association, 1990.

11. *Chem. Mark. Rep.* (Dec. 23, 1991); also author estimates.
12. “Natural Fatty Acids Report,” in *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1988.

E. T. SAUER
The Procter & Gamble Company

Related Articles

Butyraldehdyes; Carboxylic acids, trialkylacetic acids; Acrylic acid and derivatives; Carboxylic acids, fatty acids from tall oils; Carboxylic acids, manufacture; Carboxylic acid, overview; Carboxylic Acids, Branched-Chain Acids