Fatty Acids – Synthetic or Agrichemical

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ABSTRACT AND SUMMARY

The cost of producing fatty acids from agricultural products and the cost of producing them from petroleum and natural gas both depend heavily on the cost and availability of energy. The costs of the agrichemical acids and of the petrochemical acids will probably increase at the same rate in the future. Therefore, the choice of which one to use will depend at least as much on chemical composition and performance as on price.

INTRODUCTION

Agricultural and petroleum derived fatty acids have two major factors in common – a critical dependence on by-products for raw materials and on the availability of petroleum and gas. Also important to both are the price of energy, government regulations, and inflation. Most significant is the fact that both types of acids depend on having enough petroleum and gas – not just the petrochemical acids.

TABLE I

Natural Fatty Acids
(Production 1976)

	Tons	Fat Source
Stearic	160,630	Tallow and grease
	13,970	Soy and palm (tallow)
Palmitic	3,770	Tallow, palm, Lauric oils
Lauric	31,500	Coconut, palm kernel, babassu
Caprylic capric	8,350	Lauric oils
Palmitic and lauric	7,390	Lauric oils, tallow, palm
Oleic acid	132,000	Tallow (tall oil, safflower)
Linoleic, linolenic	17,650	Soybean, tall oil, safflower, linseed
Oleic-linoleic	169,730	Tall oil
Miscellaneous (behenic, arachidic, oleic, erucic)	7,600+	Fish, rapeseed, cottonseed
Grand Total	552,590+	

AGRICHEMICAL ACIDS

According to the Fatty Acid Producer's Council statistics published on February 28, 1977, fatty acids are made from agricultural raw materials by over 15 producers in the U.S. The volume is ca. 550,000 tons/per year.

Table I shows the production by types and raw materials of the most common commercial agrichemical acids.

Stearic acid types were produced in the largest volume in 1976. The biggest percentages were derived from animal fats, tallow, and grease; about 14,000 tons from vegetable oils and foots – soy and palm mainly. The oleic-linoleic mixtures were mostly derived from tall oil and in 1976 were the second largest volume produced – 169,700 tons. Oleic acid was next – primarily from tallow, some from safflower and tall oil, some as mixtures with stearic from tallow. The lauric acid types are important to this discussion. They were derived almost completely from the lauric oils – coconut, palm kernel, and babassu.

Estimates of the major raw materials used are given in Table II. Tallow was number 1 (as measured by the fatty acids produced). Tall oil was number 2. Coconut and other lauric oils were probably number 3 and soy was number 4. The numbers in parentheses in Table II were used to convert the volume data for the fats to derived acids.

The two largest raw materials are by-products – tallow and tall oil. Only the third largest, lauric oil, is a primary material. The major volumes of natural acids depend on the meat and paper industries.

Production costs for coconut type fatty acids were estimated (Table III). These are for a brand new plant on a brand new site and in 1977 dollars. Coconut oil cost accounts for 76 % of the transfer price – \$979 out of the total of \$1,296. Direct energy costs are only 2% of the transfer price. However, the coconut oil itself, the plant hardware used, transportation and selling, and administration costs are energy dependent also. The total cost of all the kinds of energy used to make coconut oil is not readily available. As an indication, about 40% of the cost of making soybean oil, for which there is more data, is highly

TABLE II

Natural Fatty acids
Major Raw Materials
1976

	Amount[a] used (Tons)	Fatty acid produced (Tons)	Sources
Tallow (90)	328,000	295,000	By-product of meat
Tall oil (25)	676,000	169,000	By-product of paper
Coconut oil (95)	53,700	51,000	Primary
Soybean oil (88)	20,500	18,000	By-product of annimal feed
Fish oils	—	—	
Palm oil	—	—	Primary
Palm kernel	—	—	Primary
Babassu	—	—	Primary
Safflower	—	—	Primary
Linseed	—	—	Primary
Cottonseed	—	—	By-product of cotton
Rapeseed	—	—	Primary

[a]Estimated.

TABLE III

Natural Fatty Acid Economics
(coconut range)

Capacity, tons	22,700
Capital, $MM	
Fixed plant	6.2
Working	4.6
Raw materials	$/ton
Coconut oil	
1.10[a]T @ $890/T =	979
Utilities	24
Labor-related	28
Capital-related	
Dep., maint., tax, ins.	49
Profit	95
Sell, adm., res.	121
Transfer price, Bulk, FOB	1296 (58.9c/lb)

[a]Glycerine credit included.

TABLE IV

Commercial Synthetic Fatty Acids

C_5	Neopentanoic (pivalic)
	Isopentanoic
	Pentanoic
C_6	2-Ethyl butyric
C_7	Heptanoic
C_8	2-Ethylhexanoic
	Isooctanoic
C_9	Pelargonic
	Isononanoic
C_{10}	Isodecanoic
	Capric
	Neodecanoic
$C_{10\text{-}20}$	Linear-terminal
$C_{11\text{-}13}$	Linear-terminal and mixed
C_{13}	Iso tri-decanoic
C_{12}-C_{15}	Linear and branched
C_{16}	Iso palmitic
C_{16}-C_{19}	Linear and branched
C_{18}	Isostearic acid
	Iso octadecanoic
C_{11}	Undecylenic

energy dependent. Also, farming in the U.S. directly uses at least 17% of all the energy consumed in the country; this includes fertilizers. More indirectly, energy is used to make agricultural equipment, trucks, tires, etc. A wild guess is that for coconut fatty acids, the energy cost is ca. 25% of the total cost.

For tallow and tall oil even less data are available at present, but they are quite dependent on petroleum and gas also.

This very broad generalization most likely gives the correct picture of how dependent agrichemical acids are on the availability and cost of energy. It is a fact that these acids are derived from renewable resources but can only be made if the required energy to plant, harvest, and process the oil is available. Costs are dependent on the cost of energy.

PETROCHEMICAL ACIDS

The commercially available petrochemical acids are listed in Table IV. About 50,000 tons are commercial now, but 91,000 tons of capacity were due on stream in July from Liquichimica's plant in Italy; however, there has been some delay. Ruhrchemie has announced an increase in capacity (on stream) to 30,000 tons. Monsanto has been making small quantities in a pilot plant and will make a decision on a commercial plant in the last quarter of this year, possibly adding another 50,000 tons of capacity. Monsanto's acids will have 11-13 carbon atoms and will consist of two grades; one is over 90% linear with terminal carboxyls. The second grade is linear also but with only about 35% terminal carboxyl groups. Monsanto is also considering including shorter chain acids, possibly for synthetic lube esters, etc.

All the above acids contain odd as well as even carbon atoms and are mostly nonlinear. The neo-types are produced by Exxon in the U.S., the iso-types by Ruhrchemie and Hoechst. The linear terminal types are produced in the USSR and China. Liquichimica will make two types, the C_{12}-C_{15} and C_{16}-C_{19} acids. They contain only about 40% linear terminal acids; the balance are branched. The iso palmitic is being offered by Henkel.

There is only one unsaturated acid in Table IV, and it is derived from castor oil. However, there are many liquid acids which can perform in many applications where unsaturated acids are now needed simply because they are liquids.

The commercially used and some potentially usable petrochemical processes are listed in Table V. Over 455,000 tons of acids are made per year. Oxidation of wax is used in the USSR and China. Oxo chemistry (hydroformylation of olefins) accounts for much of the acids. The Ruhrchemie and Hoechst processes convert olefins to aldehydes by this route. These are then oxidized to the acids. The Pechiney

TABLE V

Synthetic Fatty Acid Processes

	Commercial	Potential
Oxidation of wax – straight chain	X	
Oxidation of aldehydes	X	
Oxidation of alcohols	X	
Oxidation of olefins	X	
Hydroformylation of olefins (OXO)	X	
Carbonylation of olefins (KOCH)	X	
Ozonolysis of unsaturates	X	
Pyrolysis of castor oils	X	
Dimerization – oxidation of alcohols	X	
Fermentation		X
Carbonylation of alcohols		X
Addition of acids to olefins	?	
Oxidation of diols		X
Addition of HCN to olefins		(Unsaturated acids)
Addition of acrylonitrile to olefins		X
Addition of acrylates to diolefins		X
		(Unsaturated acids)
Telomerization of acrylates, formates, acetates with dienes		(Unsaturated acids) X

TABLE VI

Commercial Synthetic Fatty Acids
Major Raw Materials

	Sources	
	Primary	By-product of:
Propylene	—	Ethylene and gasoline
Ethylene	Natural gas, petroleum	
n-Olefins	Ethylene, petroleum, natural gas	
Iso-olefins	—	Gasoline
n-Paraffins	—	Kerosene, gas oil, petroleum wax, lub oil
Isobutylene	—	Gasoline and ethylene
Carbon monoxide	Natural gas	
Hydrogen	Natural gas	
Oxygen	Air	

TABLE VII

Tridecyl Alcohol
(by oxo process)

Capacity, tons		22,700
Capital $MM		
Fixed plant		12.5
Working		3.0
Raw materials		$/ton
Normal or α-olefin	0.93T @ $ 440/T	409
Syngas ($CO + H_2$ - 1:1 molar)	0.21T @ $ 220/T	46
Hydrogen	0.03T @ $1000/T	30
		485
Utilities		44
Labor-related		18
Capital-related		
Dep., maint., tax, ins.		99
Profit		137
		236
Sell, adm., res.		77
Transfer price, Bulk, FOB		860

TABLE VIII

Synthetic Fatty Acid
(by oxidation of tridecyl alcohol)

Capacity, tons		22,700
Capital $MM		
Fixed plant		6.2
Working		4.8
Raw Materials		$/ton
Tridecyl alcohol	1.01T @ $860/T	867
Caustic soda	0.34T @ $180/T	61
Sulfuric acid	0.33T @ $ 88/T	29
		957
Utilities		25
Labor-related		28
Capital-related		
Dep., maint., taxes, ins.		49
Profit	97	97
		146
Sell, adm., res.		121
Transfer price, Bulk, FOB		1277
Credit .44T salt cake @ $60/ton		-26
	Net	1251

TABLE IX

Synthetic Fatty Acid
(by alkaline oxidation of alcohol)

Capacity, tons		22,700
Capital, $MM		
Fixed plant	18.7	18.7
Working	4.8	4.8
Raw materials		$/ton
Normal or α-olefin	.94T @ $ 440/T	413
Syngas ($CO + H_2$ — 1:1 molar)	.22T @ $ 220/T	48
Hydrogen	.03T @ $1000/T	30
Caustic soda	.34T @ $ 180/T	61
Sulfuric acid	.33T @ $ 88/T	29
		581
Utilities		69
Labor-related		46
Capital-related		
Dep., maint., taxes, ins.		148
Profit	234	234
		382
Sell, adm., res.		150
Transfer price, Bulk, FOB		1231
.44T salt cake credit, @ $60/ton		26
	Net	1202

TABLE X

Synthetic Fatty Acids
(by oxo carbonylation)

Capacity, tons		22,700
Capital, $MM		
Fixed plant		21
Working		4.2
Raw materials		$Yton
α-Olefin	440	405
Carbon monoxide	220	29
Catalyst and chemicals		22
Utilities		18
Labor-related		24
Capital-related		
Dep., maint., tax, Ins.		167
Profit		222
Sell, adm., res.		100
		987
Credit[a]		(40)
Transfer price, Bulk, FOB		947 (43c/lb)

[a]Recovered hydrocarbons .136T @ $319/ton.

Ugine Kuhlmann process converts to the aldehydes or alcohols which are then oxidized to the acids. All the iso acids except isostearic and isopalmitic are made this way.

Ozonolysis is an important process (pelargonic acid). Koch chemistry is used for neo acids. The Liquichimica process is based on the oxidation of alcohols with caustic.

The Monsanto process converts olefins in one step to acids by oxocarbonylation chemistry. This technology appears to be viable technically and economically. The project now has tentative approval to proceed with significantly increased effort.

The major raw materials are derived primarily from petroleum and gas (Table VI). The classification into primary and by-products is arbitrary but does illustrate the interdependence of the commercial acids with basically by-product raw materials.

All the major raw materials are 100% energy dependent; all except oxygen are fuels that are also feedstocks for the

TABLE XI

Fatty Acids

Capacity, tons		22,700	
	Natural	Synthetic by alcohol oxidation	Synthetic by oxocarbonylation
Capital, $MM			
Fixed plant	6.2	18.7	21
Working	4.6	4.8	4.2
Raw materials	$/ton	$/ton	$/ton
Coconut oil @ 890	979	---	
C_{12}-olefin @ 440	---	413	405
Others	---	168	22
Utilities	24	69	
Labor-related	28	46	18
Capital-related			24
Dep., maint., tax, ins.	49	148	167
Profit	95	234	222
Sell, adm., res.	121	150	100
Transfer price, Bulk, FOB	1296	1231	987
Credit		-26	-40
Net		1202	947
	59c/lb	55c/lb	43c/lb

TABLE XII

Price Projections

	1976 $/ton	1987 $/ton	Growth rate %
Crude oil	78	202	9
Natural gas	94	223	9
Naphtha	114	271	9
Gas oil	71	184	10
Gas liquids	100	259	10
Ethylene	264	578	8
Propylene	200	432	8
α-Olefins	440	950	8

TABLE XIII

Fats and Oils Prices

	1967 $/ton	1976 $/ton	1977 $/ton
Tallow (BF)	121	330	440
Coconut oil	297	506	850
Soybean oil	231	462	660
Tall oil fatty acids (<2%)	220	528	528

acids. However, farm products on which agri-fatty acids are dependent also would probably not be available in the current quantities and at the current prices without the same fuels.

Internal transfer prices for coconut range synthetic acids were estimated for a 22,700 ton plant, based on a brand new plant on a brand new site and 1977 dollars. The estimates were based on using the oxo process to make the alcohols (Table VII) followed by caustic soda oxidation to produce the acids (Table VIII). This resembles the reputed Liquichimica process, but the estimates apply only to one set of U.S. conditions and situations and are not intended to apply to Liquichimica in Italy. The costs shown are useful for comparing petrochemical acid economics with those for agrichemical acids. In Table IX, the effect on costs of integrating the manufacture of the alcohols and acids was estimated.

It is significant that 55% of the costs are entirely energy – the olefins, carbon monoxide plus hydrogen, hydrogen and utilities. This is in contrast to the ca. 25% for agri-acids.

Using a one-step conversion of olefins directly to acids can reduce costs of production (the internal transfer price) considerably using the same olefin prices (Table X). Capital is higher than in the two-step process, but raw materials are less. Fuels are ca. 50% of the transfer pice. The one-step process costs are $947/ton vs. $1,202 for the two-step process.

It is obvious (Table XI) that synthetics could be competitive with $890/ton coconut oil. There are several major factors that can lower costs for all processes: size of plants (the scale), pricing the raw materials at by-product values vs. alternate use values, use of government funds at very little cost, and government regulations. These cost estimates assume 100% sale of product on day one of startup and excellent luck for startup. These are brand new processes and products vs. agri-acid processes which are well experienced and agri-acids which are well known. Cost/performance will have a major influence on their relative values. Natural acids are, of course, linear, even carbon numbered, terminal carboxy acids. The synthetics for which the costs are given are mixtures of odd and even carbons, and are mostly not linear.

Both Monsanto and Liquichimica have maintained that their products could be priced competitively with coconut acids when the latter were $900/ton. Currently coco acids are listed in the $1,254 – $1,320/ton range, as published in the *Journal of Commerce,* April 27, 1977. The estimated transfer price in Table XI is $1,296.

DISCUSSION

The relationship of the costs for the two types of acids in the future is hard to forecast. There are some signals that indicate synthetics will become more important to industry.

Over the nest 10 years petroleum and gas prices are projected to go up, somewhat like in Table XII. The forecasts are in current dollars and assume a 6% inflation rate. All forecasts made in today's environment are highly uncertain, unfortunately.

Table XIII lists the historical average prices for fats and oils. Data were provided by the USDA. The 1977 prices are the maximum for the first 4 months of the year.

Coconut oil has been forecast by the World Bank (Private communicaton, May 5, 1977) to go from about $450/ton in 1975 to $755/ton in 1980. This price was adjusted by the author from the listed Rotterdam CIF basis to U.S. delivered. These are all current dollars. At this rate – ca. 11% with inflation @ 6% – the price in the U.S. might be about $1,100 – $1,200 by 1985.

Coconut oil is an important primary fat and also an important target for replacement by synthetic fatty acids.

There are no available expert forecasts for tallow. A growth rate of ca. 8%/year is probably a good educated guess – just 2% over the expected inflation rate. The price could be $660/ton by 1985. All prices are in current dollars (i.e., the dollar's value in the year given). Therefore, prices for both agri and petro raw materials could be up by a factor of ca. 2. This could be interpreted as a slight pitch in the favor of agri-acids. But, synthetics are already in the marketplace quite significantly and have a chance of breaking through into much larger volumes. Both types of acids have their places in the market – on performance and cost.

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