Background, Importance and Production Volumes

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ABSTRACT

The importance of the fatty acid industry today is reflected by the estimated 1978 production in the U.S. of 956 $\overline{M}$ lbs., exclusive of tall oil fatty acids. The 1978 U.S. production of various fatty acids as reported monthly and annually by the FAPC of SDA, is broken down into 9 saturated categories, and 5 unsaturated categories, as follows: (1) stearic and 127.2 $\overline{M}$ lbs. (13.3%); (2) hydrogenated animal and vegetable acids (2a) 97.3 $\overline{M}$ lbs. (10.2%), (2b) 158 $\overline{M}$ lbs. (16.5%), (2c) 32 $\overline{M}$ lbs. (3.4%); (3) high palmitic, 14.6 $\overline{M}$ lbs. (1.5%); (4) hydrogenated fish, 6.5 $\overline{M}$ lbs. (0.7%); (5) lauric acid types, 88.8 $\overline{M}$ lbs. (9.3%); (6) fractionated fatty acids, (6a) C_{10} or lower, 18.5 $\overline{M}$ lbs. (1.9%), (6b) C_{12} and C_{14} 55% 17$\overline{M}$ lbs. (1.9%); (7) oleic acid, 158.3 $\overline{M}$ lbs. (16.6%); (8) animal fatty acids other than oleic, 156.3 $\overline{M}$ lbs. (16.3%); (9) vegetable or marine fatty acids, 0.1 $\overline{M}$ lbs. (less than 1%); (10) unsaturated fatty acids, 57 $\overline{M}$ lbs. (6.0%); (11) unsaturated fatty acids I.V. over 130, 24.2 $\overline{M}$ lbs (2.5%). Reported 1977 fatty acid derivative production from fatty acids (not fats and oils) is 1,980 $\overline{M}$ lbs. The average price of fatty acids has increased from 23¢/lb. to 60¢/lb. within the last 5 years.

It is not too unreasonable to say that fatty acid production is older than Adam, as the process by which fat is metabolized by men and animals is the hydrolysis, or splitting, of fatty glycerides. Animal and vegetable fats and oils are of course older than recorded history; for centuries man used them in a variety of ways besides as foods.

Vegetable oils were used by the Egyptians and Phoenicians for anointing their bodies but not for illumination. According to one authority, earthen vases believed to predate the First Dynasty, about 3200 BC, were found to contain fatty materials. One contained a brown granular substance identified as palmitic acid mixed with tripalmitin. This probably had originally been palm oil which had undergone oxidation and partial saponification. Another vase contained a more granular, paler mass consisting of stearic acid with about 30% tristearin. This had probably originally been beef or mutton tallow. These materials were probably intended as provisions for the dead. It's an interesting question as to whether they were meant as food or as a way to "grease" their way into the next world.

Apparently, the Egyptians used olive oil as a lubricant for moving large stones and other building materials, and according to one authority, axle greases of that time consisted of a fat mixed with lime and other materials and were used in the Egyptian chariots as early as 1400 BC.

"Introduction to the History of Science," written over 50 years ago, contains numerous references to the use of fats and oils in the arts, technology, and medicine from the ninth and eighth centuries BC to the middle ages. Homer refers in his poems to the use of oil in weaving, and candles made of beeswax and tallow were known to the Romans. The chances are that others in pre-Roman times did the same.

One of the larger uses of fats in modern civilization, the manufacture of soap, goes back for centuries. The Phoenicians made soap as early as 600 BC and used it as an article of barter with the Gauls. It is not known whether the Romans learned the use of soap from the ancient Mediterranean peoples or the Celtic inhabitants of Britannia who produced soap from fats and plant ashes and gave the product the name "saipo," from which the word soap is derived.

Soap as both a medicinal and a cleaning agent was known to Pliny (23-79 AD), who mentioned both hard and soft soap, and the chances are that soaps were known considerably prior to Pliny's time. According to Pliny, soap appears to have been made by boiling goat tallow with causticized wood ashes to produce a soft soap by repeatedly treating the pasty material with salt or sea water. Excavations at Pompeii, destroyed in 79 AD, have revealed at least two buildings equipped as soap factories.

Galan, the Greek physician, refers to soap as a medicament and body cleansing agent and others of like periods mention it as a shampoo.

A compendium of arts of the late eleventh and early twelfth centuries includes extensive detail on the preparation and use of oil colors by the use of linseed oil with some type of resin. It was not until the fifteenth century that the effect of driers in linseed oil paints was discovered.

Another and very different early use of oils was their application on water surface to subdue the waves during a storm. This phenomenon of surface tension or extension of oil upon the surface of water was investigated by a Hindu mathematician in the middle twelfth century. It is interesting to note that modern science is still studying this—not to calm rough seas, but to decrease or lessen water evaporation from reservoirs.

Still primitive but more modern civilizations such as those of the Indians of North and South America were familiar with many oil-producing plants and employed them as food, medicine, cosmetics and illuminants. It has been reported by researchers that the Indians of Panama strung oil-rich nuts on splinters of wood and used them as candles, and in Brazil and other parts of South America various species of oil palm were similarly used.

From these examples we must conclude that man has been familiar with fats and some of their properties from prehistoric times. Long before he had any knowledge of the chemical nature of these substances, he apparently recognized differences in their properties and employed them in a variety of ways. Their use as foods was probably instinctive, but other uses must have resulted from observation of the properties and behavior under various environmental conditions. Methods for their separation must have been devised before the dawn of history.

Fats of animal origin were probably the first fats used by man, and these were separated from other animal tissue by heating or boiling with water. Oily fruits such as olives, oil palm and avocado, and oil-rich nuts were probably made to yield their oils in the same manner. In the oil palm belt of Central Africa, as well as in Brazil, the natives still produce oil by boiling the fruit of the oil palm with water after preliminary fermentation and maceration of the pulp. In the western hemisphere, the natives of many parts of Central and South America produced oils from various palm and other oil-rich nuts by crushing the kernels, roasting the crushed mash and boiling it with water, a practice which may still be used in isolated South America.

Recovery of oil from small seeds with extremely hard coats required more vigorous methods of processing which involved cooking, grinding and pressing methods. But again, these are of very ancient origin. The Hindus manufactured cotton fabric and crushed cottonseed for oil and cake in the fifth century BC.

The Hebrews possessed oil mills powered by treads that were usually operated by prisoners. Sesame, linseed and castor oils were produced in Egypt by pressing as early as 2½ centuries BC, and screw and wedge presses, filters and edge runner mills were used in Rome for the production of oil as early as 184 BC.

Pliny the Elder described olive, rice, almond, sesame, grapeseed, walnut and palm oils, and an olive oil mill which resembled the edge runner. This machine had stones that were flat on the inner side and convex on the outer side. The Greeks and Romans are said to have employed screw presses, similar to wine presses for recovering olive oil, and the wedge press was used in very early times in the Orient, particularly China, where it is still operated.

Prior to the beginning of the nineteenth century, the use of fats and oils was based on empirical knowledge accumulated over many centuries, while today's uses stem largely from a knowledge of composition, structure, properties and reactions of the component fatty acids.

Early in the era of modern organic chemistry Scheele obtained glycerol by heating olive oil with litharge. In 1813, Chevreul began his researches on fats which he describes in his classic work "recherches Chimique sur les Corps Gras d'Origine Animale." He isolated butyric acid from butter, established the glyceride nature of fats, and prepared stearic, valeric, caproic and impure oleic acids.

In 1829, Lefevre observed that tallow could be treated with sulfuric acid to yield fatty acids, and through the first half of the nineteenth century it was learned by various workers that sulfonated oil could be produced, that fusion of oleic acid with caustic soda gave palmitic and acetic acids, and erucic acid was isolated. Berthelot demonstrated during the 1850s the trihydric nature of glycerol, and synthesized the first nonglycerol polyhydric alcohol esters. He synthesized mono- and diglycerides and suggested that natural fats consist of mixtures of heteroglycerides rather than mixtures of homoglycerides.

During the latter half of the last century, little progress was made in the fundamental chemistry of fats and fatty acids, but many useful analytical tests were developed which would be applicable. Also, new and efficient methods of saponification were introduced as was the vacuum distillation of fatty acids and glycerol and the solvent extraction of fats. Turkey red oil was prepared by sulfonation of castor oil, and margarine and linoleum were invented and produced commercially.

During the latter nineteenth century, fats were not the subject of investigation by chemists. Their use in industry was in foods, soap making and in the manufacture of paints and varnishes. From the academic point of view, they were not considered attractive research materials as they were not crystallizable and few crystalline derivatives could be prepared from them. They were considered very simple substances and were assumed to possess few characteristic chemical or physical properties, and finally they could not be separated into definite chemical entities by any simple method such as crystallization or distillation.

The fatty acids were known to consist of a relatively long saturated or unsaturated hydrocarbon chain with a terminal carboxyl group. It was assumed that such simplicity of structure offered little opportunity for applying newly discovered reactions which were being used in petroleum chemistry.

Two men are probably responsible more than any others for reviving an interest in fat chemistry. T.P. Hilditch of the University of Liverpool and George S. Jamieson of the U.S. Department of Agriculture, both of whom carried out a wide area of research on fats and fatty acids and published a series of books and monographs which organized and systematized the accumulating knowledge in the field (1–3). They investigated many heretofore little known fats and clarified the composition of these and more well known fats and contributed new techniques of analyses.

The first quarter of the twentieth century also saw the founding of new scientific societies and journals devoted to the interests of scientists specializing in the chemistry and technology of fats and oils and their derivatives. The AOCS was formed in 1909 and what is now published as the Journal of the AOCS was from 1917 to 1924 published as the Chemists' Section, Cotton Oil Press. From 1924 to 1931 it was titled Oil and Fat Industries, and from 1932 to 1947, Oil and Soap.

During the second quarter of the century, special laboratories and institutes were established which were largely or exclusively devoted to research on fats and oils.

During the last fifty years, the production and utilization of fatty acids has grown both in size and diversity. While closely allied with the fats and oils industry, it has become today a separate and distinct industry. Compared with the fats and oils industry whose origin is lost in antiquity, the fatty acid industry is of comparatively modern origin going no further back than the work of Chevreul from 1811 to 1825 on the saponification of fats and the isolation and identification of various acids including stearic and oleic. This work culminated in the issuance of a French patent to Chevreul and Gay-Lussac in 1825 for the separation of fatty acids and their utilization in the manufacture of candles.

The work which was the basis of the French patent was soon after applied to the production of stearin and red oil, terms applied to what we know today as crude stearic and crude oleic acids. They represented little more than the separation of the mixed fatty acid of saponified inedible tallow into liquid and solid fractions, or unsaturated and saturated, by a method known as pressing and panning.

Commercially, the process of fat splitting emerged in the middle of the nineteenth century as the result of demand for improved candles, made possible when stearic acid was substituted for the whole tallow. Originally it was necessary to make a lime soap from the fat which could be acidulated to yield the mixed fatty acids. The liquid acids, largely unsaturated, were separated from the solid by pressing. The stearic acid was used with paraffin to improve the burning quality of the candles.

The red oil or liquid fraction which was produced simultaneously with the solid stearic fraction found use as textile lubricants and in the manufacture of soaps for various textile applications, for manufacturing greases and the production of sulfonated red oil.

The original panning and pressing method, with many modifications and improvements, is still used extensively, but during the first half of this century other methods including distillation and solvent fractionation were introduced for separation of fatty acids. In 1870, the first patent was issued for the recovery of glycerol by distillation, and in 1882 glycerol was refined by vacuum distillation.

It was about 1900 that Twitchell developed the soon to be famous Twitchell Reagent for splitting fats chemically, using hot water and steam in contact with the fat in the presence of about 1% of an aromatic sulfonic acid catalyst.

None of these processes was applied on a large scale for the separation of fatty acids until the present century when industrial demand arose for fatty acids other than oleic and stearic.

In response to these demands, fatty acids from cottonseed, soybean, corn, coconut and palm kernel oils came into use by the industry. These products were unfractionated or crudely fractionated mixtures produced by distillation in relatively crude stills. A further demand arose for relatively homogeneous individual acids which in turn led to the development of improved methods of splitting, separation, hydrogenation and distillation to produce the entire series from C_6 to C_{22}.

Since the original studies of Chevreul in 1823 on saponification of animal fats and separation of fatty acids, an industry has developed which involves investment of millions of dollars in plants and equipment and produces

TABLE I

Production of Saturated Animal and Vegetable Fatty Acids
In Millions of Pounds

	1971	1978
1. Stearic acid 40–50%	79.5	127.2
2a. Hydrogenated fatty acid titer 60 C max. i.v. 5 min.	100.5	98.1
2b. Hydrogenated fatty acid titer >57 C, i.v. <5	99.3	158.5
2c. Hydrogenated fatty acid min. 70% stearic	21.3	32.3
3. Palmitic min. 60% i.v. 12 max.	5.4	14.7
4. Hydrogenated fish fatty acids	10.3	6.5
5. Whole coconut type acids	48.6	88.8
6a. Fractionated short chain C_{10} or lower	10.2	18.5
6b. Fractionated lauric or myristic content 55%	24.4	16.8
Total saturated	399.5	561.4

Production of Unsaturated Animal and Vegetable Fatty Acids
In Millions of Pounds

	1971	1978
7. Oleic acid	126.7	158.3
8. Animal acids other than oleic i.v. 36–80	39.2	156.3
9. Vegetable or marine acids i.v. max. 115	4.5	0.1
10. Unsaturated acids i.v. 116–130	15.0	57.0
11. Unsaturated acids i.v. over 130	9.9	24.2
Total unsaturated	195.3	396.1

close to a billion pounds a year of fatty acids in the United States.

The growth of production of saturated and unsaturated acid production during the twenty-six years that the Fatty Acid Producers' Council has been collecting this data is shown in Table I. In 1952 production as reported to the FAPC amounted to a total of 365 million pounds. This has increased at a comparatively steady rate until production in 1978 amounted to 957 million pounds. These figures represent production of animal and vegetable acids and do not include tall oil fatty acids. While the figures on this chart from 1952 to 1972 may be somewhat distorted due to the limitations of space, the growth flow over these years could be said to reflect industrial activity. Figure 1 illustrates the parallel of fatty acid production to U.S. Industrial Production as reported by the U.S. Bureau of Economic Analysis, and to U.S. Chemical Industry Production, as reported by the same source. The U.S. Industrial Production figure includes categories of production in SIC codes 20 to 39. The obvious reason for this parallel is the fact that fatty acids are used in thousands of products produced by American industry either as acids or as derivatives. As is also obvious from this figure, when business is good, generally the production of fatty acids rises. The famous or perhaps infamous recession of 1975 is reflected in the sheer drop not only for fatty acid production but for chemicals as a class and industrial production generally. While on the subject of production levels, perhaps we should look at the 1978 production and the breakdown of types of acids that comprises the total as shown in Figure 2. Total figures for 1978 are compared with only six years ago. In that time, production has grown from just short of 600 million pounds to almost 960 million pounds or a growth of better than 60%. Some categories have grown more than others but the percentages don't vary much.

The fatty acid industry has a number of natural products which they use as raw materials–tallow, coconut oil, soybean oil, fish oil, palm oil, and vegetable oil foods. But the dominant and most important are, of course, tallow and coconut oil. The latest year for which the Department of Commerce has issued figures, 1977, indicates a consumption of tallow in fatty acid production at 834 million pounds. This is the second largest domestic use for tallow, exceeded only by its use in animal feed. Coconut oil consumption by the fatty acid industry in the same year was 107 million pounds. From this it must follow that the industry health to some extent relies on the tallow and coconut oil markets.

From 1952 to 1957, the price of tallow ranged from 4.4 cents/lb to 7.4 cents/lb, and coconut oil from 13.6 cents/lb to 19 cents (4). Today inedible tallow is quoted (5) at 26–27 cents/lb. Coconut oil has risen during the same period but not at the same rate. Today it is quoted at about 47 cents. The percentage of increase is not as large as that for tallow.

The selling price of the acids has escalated over the past 25 years. Oleic acid during the same period of the fifties was quoted at an average of 15 cents/lb and stearic at 16½ cents (6). Today oleic acid is quoted at 46–58 cents and stearic at 36–50 cents depending on grades and quantities· (7).

While raw material costs are one larger factor, other aspects must be included. The first of these is energy costs. No one needs to be told that these have risen dramatically in recent years. In cold weather, the raw materials and acids must be kept at a temperature that permits pumping and handling. In hot weather the reverse holds true in that both raw and finished product must be at a "handleable temperature." To this cost is added the thermal heat required for conversion from fat or oil to the acid. Another factor in costs would be transportation. Overall the fatty acid industry would probably be considered an energy intensive industry.

While the price of raw materials is a major governing factor, the cost of processing must also be reflected in the finished product. A study of the industry made in 1975 put the cost of processing at 0.45 to 0.73 cents/lb for splitting, 0.57 cents/lb for distillation, and 1.66 cents/lb for separation (8). Inflation has probably doubled these figures in the past 4 years.

The effects of labor costs, while important, probably do not have the same impact. More and more the fatty acid industry has become automated over the years. In the early days when panning and pressing was the major operation of a fatty acid plant, it required a comparatively large labor force to carry out the operation. With modern methods of production this requirement for manual operation has diminished.

Another factor in the fatty industry is the automatic production of the coproduct glycerin. In some ways, glycerin might be said to be partly responsible for the modern development of the fatty acid industry. During World War II, the demand for glycerin in explosives and surface coatings prompted regulations that limited the use of fat in soapmaking processes in which glycerin was not recovered. These regulations forced some soapers to buy fatty acids rather than whole fats as raw materials for their products. In turn, the manufacturers of fatty acids found that by starting with a relatively pure fatty acid, more uniform products could be produced, and the trend has persisted, even though the demand for glycerin has somewhat diminished. It still finds applications in hundreds of products, most notably alkyd resins, tobacco processing, drugs and cosmetics, urethane foams, foods and cellophane. So the market price for glycerin must also be figured into the profit and loss picture in the fatty acid industry.

There are fifteen producers of fatty acids (animal and vegetable) in the U.S. But to the rest of the business community, it is not a singular group of companies with an individual technology such as the petroleum industry or the pharmaceutical industry. For example, there is no comprehensive SIC Code classification for the fatty acid industry or the derivative industry, and the tariff schedules of

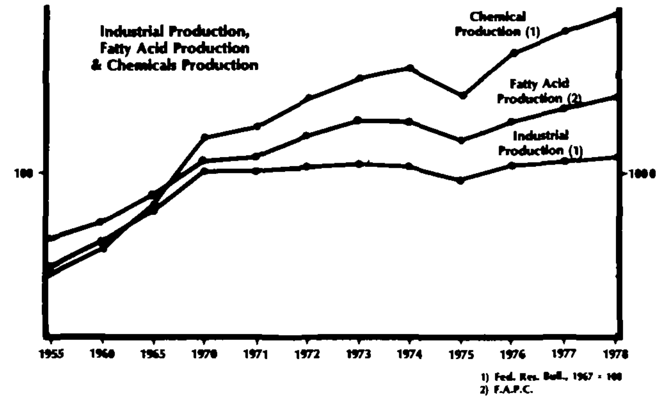

FIG. 1. Parallel of fatty acid production to U.S. industrial production.

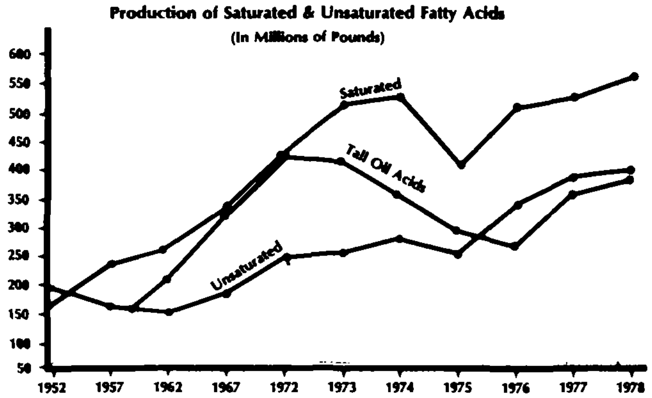

FIG. 2. Fatty acid production of 1978.

the U.S. for imports of acids and derivatives are today, to say the least, convoluted and conflicting.

The company that produces *only* fatty acids and fatty acid derivatives is the exception today, rather than the rule. For the most part they are divisions or subsidiaries of larger corporations. Perhaps part of this is due to the scope of applications of the acids themselves and the even wider scope of derivative applications. It has been estimated (4) that no one field of use represents more than 20% of the total one billion pounds consumed in 1978. It should be pointed out that the figures shown for production are fatty acids produced for merchant sale or captive use, and do not reflect acids produced as part of a continuous soapmaking process. This diversity of markets can have its own problems. The costs of keeping abreast of uses, technology, and marketing in all the possible fields of application are high for the dollar volume involved. Developmental and technical departments, operating independently of sales staffs, offer new fatty chemicals for experimental use with the objective of breaking into new markets.

Fatty acids in today's markets find their way into thousands of uses and probably most of these uses are via derivatives. The diversity of end use applications is partially explained by the relatively low cost of commercial fatty acids, their physiological compatability with animals and humans, availability of raw materials and the highly functional surface activity of the derivatives. For example, grease is merely petroleum oil until 1% to 5% of fatty acid soap is added; rubber compounds do not vulcanize properly until about 1% of stearic acid is added; 0.15% of a fatty acid-derived emulsifer in bread minimizes variations in texture and volume and provides antistaling properties. Nitrogen derivatives of fatty acids are even more dramatic in their surface active properties–0.25% of a fatty acid amine provides corrosion resistance in secondary oil recovery and only parts per million of a fatty acid quaternary maintain control of sulfate-reducing bacteria in the same process. A very small amount of fatty acid amine will function as an additive in automobile gasoline, and an equally small quantity of a fatty acid quaternary will soften and render static free 80 pounds of dry laundry.

Expansion of the fatty acid derivative market has over the years tended to change the nature of the fatty acid industry from fat splitters to chemical compounders. It has been estimated, in one study, that there are 26 or 27 sharply defined end uses for fatty acids and seven main classes of derivatives. In 1952 when the FAPC started collecting its data on production and disposition of fatty acids, 14% of annual production was used captively by the reporting companies. In 1978, 30% of production was reported as being used captively to make derivatives. Or, more specifically, in 1952 the captive use was 51 million pounds, in 1978, 290 million pounds.

What in essence is an old industry continues to grow and serve many valuable and diverse speciality end uses today. New uses continue to be found. Raw materials are replenishable and probably will be expanded; they are often byproducts and often interchangeable. The industry has grown and should in future continue to grow and find new outlets.

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Vegetable Oil Raw Materials

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ABSTRACT

Vegetable oils that are important to the chemical industry include both edible and industrial oils, which contribute 24% and 13.5%, respectively, compared to 55% for tallow, to the preparation of surfactants, coatings, plasticizers, and other products based on fats and oils. Not only the oils themselves but also the fatty acids recovered from soapstock represent a several billion pound resource. Coconut oil is imported to the extent of 700-1,000 million pounds per year. Its uses are divided about equally between edible and industrial applications. Safflower oil has a