Animal Fat Feedstocks for Oleochemicals

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ABSTRACT

Inedible tallow is a major raw material source in the manufacture of fatty acids and hence in the production of oleochemicals. The U.S. generates about 55% of the world's total tallow production of six million metric tons, but supplies about 80% of the tallow imported by other countries. U.S. inedible tallow and grease usually is a blend whose principal component is rendered beef fat. It consistently has been and still is the least expensive of the various fats and oils and is traded in various grades depending on physical characteristics.

INTRODUCTION

The use of animal fats as feedstock for oleochemicals appears to have a history of more than 5000 years. Markley (1) quotes sources that report the finding of earthen vases in Egyptian tombs believed to predate the First Dynasty (ca. 3200 B.C.). One of these vases contained a solid that was high in stearic acid and was believed to have been beef or mutton tallow, while another contained a fatty material mixed with galena (PbS), which probably was used as a cosmetic. The Egyptians also are reported to have used mixtures of fats and lime as axle grease for their chariots as early as 1400 B.C. Soap was made by the Phoenicians as early as 600 B.C., and candles made of beeswax and tallow were known to the Romans and probably were used by others in pre-Roman times. Excavations at Pompeii, which was destroyed in 79 A.D., showed that the town contained at least two soap factories. Numerous other examples could be quoted illustrating the use of fats and waxes by early civilizations to manufacture protective and decorative coatings, soaps, cosmetics, medicinals, lubricants, etc., but it is not necessary to belabor the point. The purpose of this review is to survey the present position of the use of animal fats as raw materials for chemical uses. This will be supported by a summary of recent trends of the marketplace and of recent technological advances that have led to the current situation.

The world's production of fats and oils continues to increase at a yearly rate of 3-3.5% and is estimated to have reached a level in excess of 64 million metric tons in the 1982/83 production year (Table I). The worldwide production of animal fats, which includes butter, lard, edible tallow and inedible tallow and grease, remained fairly constant over the 3-yr period indicated and constituted a little over 25% of the total fats and oils supply. World production of tallow and grease was quite constant over the three production years ending in 1982, at about 6 million metric tons (Fig. 1), and U.S. production, also constant, has been about 55% of the world's total. The impact that U.S. production of tallow and grease has on world markets is, however, much larger than one would suspect from its 55% share of production. Forty-four countries have been listed by the USDA Foreign Agricultural Service as having produced some amounts of tallow and grease in calendar year 1980. Those which produced at least 200 thousand metric tons are listed in Table II, along with their exports and imports. They account for 87% of the tallow and grease produced in the world. The picture that emerges from this table is that there are only four countries which are net exporters and that the United States supplies about 80% of the tallow and grease imported by others.

In 1983, the United States exported tallow to 57 countries (3). It is interesting to look at the list of the 12 largest customers and at the change that has occurred over the past 10 years (Table III). In 1973, Japan bought more U.S. tallow and grease than any other country; but by 1983, it had dropped to seventh on the list, and its U.S. purchases had been reduced by almost 75%. Japan produces significant quantities of soap, fatty acids and fatty acid derivatives. Its decreased purchases of U.S. tallow have been offset by increased imports of tallow from Australia and by increased utilization of palm oil as a raw material source. In 1983, Egypt had replaced Japan at the top of the list of U.S. tallow customers. Neither Egypt nor the other countries at the top of the list, with the exception of the Netherlands, have exceptionally strong industrial bases. Perhaps these countries

TABLE I

World Oil and Fat Production (2) (in million metric tons)

Source	1979/80	1981/82	1982/83 (Provisional)
Liquid oils	32.99	33.98	35.75
Palm type oils	8.20	9.34	9.75
Industrial oils	1.36	1.18	1.29
Animal fats	16.80	16.58	16.61
Marine oils	1.20	1.18	1.13
Totals	60.55	62.26	64.53

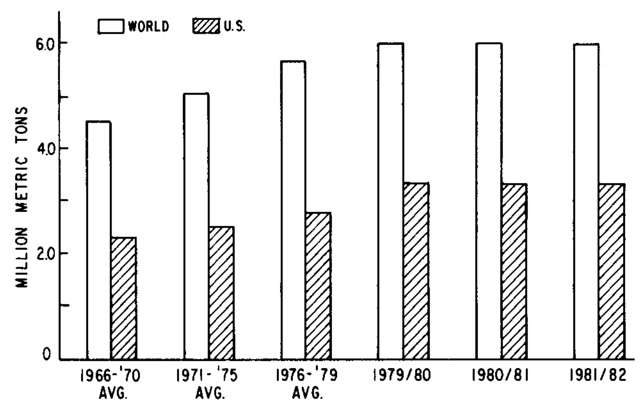

FIG. 1. Tallow and grease production 1966-82. Source: Foreign Agricultural Circular FL & P 2-82, USDA, Sept. 1982 and FOP 11-82, USDA, Sept. 1982.

TABLE II

Tallow and Grease Production by Country (1980) (in thousand metric tons)

	Production	Export	Import	Net export
USA	3,157	1,520	–	1,520
Soviet Union	340	–	52.0	–
Australia	309	181	–	181
Argentina	308	58	–	58
Germany (Fed. Rep.)	235	142	172	–
United Kingdom	235	8	102	–
France	220	44	68	–
Canada	204	166	5	161
Brazil	200	–	68	–

Source: Foreign Agricultural Circular FL & P 2-82, USDA Sept. 1982.

TABLE III

U.S. Exports of Tallow and Grease—Countries of Destination (thousand metric tons)

	1983[a]	1973[b]
Egypt	226.9	64.7
Netherlands	125.2	113.0
Pakistan	83.8	26.0
South Korea	81.0	86.3
Mexico	70.7	17.3
Colombia	64.5	23.7
Japan	56.4	197.5
USSR	54.5	N/A
Spain	40.8	55.9
India	39.2	16.8
W. Germany	36.6	39.8
Taiwan	36.5	15.0

Sources: [a]Ref. 3; [b]Ref. 17.

purchase tallow primarily for conversion to soap and for utilization in animal feeds.

Tallow and lard are both byproducts of the meat industry. Lard is an edible fat obtained from hogs, and edible tallow usually is derived from beef fat. Inedible tallow, also known as industrial or technical tallow, includes tallow and greases, and usually contains fats derived mainly from cattle, but also from hogs, sheep and poultry. The distinctions between edible and inedible tallow are based on hygienic and regulatory considerations rather than on chemical differences. To be classified as edible, the tallow must be derived from clean, sound tissues from carcasses of animals that were in good health at the time of slaughter. Furthermore, the production of edible tallow must proceed under hygienic conditions and under constant regulatory supervision. The amount of edible tallow produced in the U.S. for many years was fairly constant at ca. 0.25 million tons. In recent years, it has more than doubled; it constituted about 17% of the total amount of tallow produced domestically in 1983 (3).

In contrast to edible tallow, the inedible material is classified and traded in various grades in which minimum melting point (titer), maximum color, free fatty acid content and other physical properties including MIU (moisture, insolubles and unsaponifiables) are specified, rather than their origin, as seen in Table IV. The lower grade materials are, of course, also the least expensive and the most variable in terms of chemical homogeneity, uniformity of source and type of prior treatment. Because of their lack of uniformity from batch to batch, these less expensive grades present difficult technical problems to the chemical manufacturer who wishes to use them as feedstock. For many applications, these materials cannot be considered, because the expense of product purification is greater than the raw material price differential.

The prices of fats and oils have a tendency toward periodic fluctuations, as do other commodities. If one plots the yearly average price of each of the various fatty commodities against time (4-6) one obtains a series of parallel traces in which tallow is represented by the bottom or lowest priced curve. The parallel nature of the curves stems from the fact that the major fats and oils are fairly similar in their major composition, and there is a good bit of interchangeability among oils for various uses.

To the producer of fatty acids, the origin, composition and quality of the raw material used has a bearing upon the composition and quality of the fatty acids that can be produced from it. Composition of animal fats depends on a number of factors, such as source animal, history of the animal (breed, age, sex, feed), history of the fat and external contaminants.

TABLE IV

Standard Grades, Specifications and Quality Tolerances for Tallows and Greases[a]

	Specifications			
Grades	Titer min	FFA max	FAC max	MIU
Edible tallow	41.0	0.75	3	*
Top white tallow	41.0	2	5	1
Extra fancy tallow	42.0	2	5	1
Industrial extra fancy tallow	41.0	3	5	1
Fancy tallow	40.5	4	7	1
Bleachable fancy tallow	40.5	4	none	1
Prime tallow	40.5	6	13-11B	1
Special tallow	40.5	10	19-11C	1
No. 1 tallow	40.5	15	33	2
No. 2 tallow	40.0	15	none	2
Intermediate special tallow	39.0	10	21	1
"A" tallow	39.0	15	39	2
Choice white grease	36.0	4	13-11B	1
Yellow grease	36.0	15	37	2

[a]Official American Fats and Oils Association export grades.
*Moisture maximum 0.20%. Insoluble impurities maximum 0.05%.

TABLE V

Major Fatty Acids of Some Depot Fats (wt %) (18)

	14:0	16:0	18:0	16:1	18:1	18:2
Frog	4	11	3	15	52	52
Crocodile	3	27	5	7	34	17
Rabbit	7	32	5	5	28	19
Horse	5	26	5	7	34	5
Hippopotamus	4	27	21	5	38	3
Camel	5	31	31	4	28	1
Lion	5	29	18	2	40	–
Human	3	23	4	8	45	10

The principal components of all animal fats are triglycerides, which are esters of fatty acids and the triol glycerol. With few exceptions, we know little about the specific triglycerides present in fats, except that they are numerous. When our interest focuses on the fatty acids themselves, we simplify the analytical problem by converting the triglycerides to methyl esters and analyzing these by some chromatographic procedure. This gives us an idea of the relative amounts of fatty acids present, not only in the triglycerides but also in other components of the fat. The fatty acid composition of a very large number of tissues has been determined over the years, from microorganisms through insects and marine and land animals through human lipids. Not only the depot fats, but also the lipids present in animal and human organs, body fluids, structural parts and other components have been analyzed, and their principal fatty acid compositions have been recorded. The data of Table V illustrate the type of information available. Even more detailed data on lipids from animal and plant tissues can be gleaned from Hilditch and Williams (7), and animal fats of industrial importance are discussed in Bailey's Industrial Oil and Fat Products (8). The development of gas chromatographic methods during the past 25-30 years has aided tremendously in advancing the state-of-the-art of fatty acid analysis. In fact, the composition of lipids can be measured more precisely and more rapidly now than that of any other natural product. Furthermore, the details of information available on fatty acid composition are still evolving

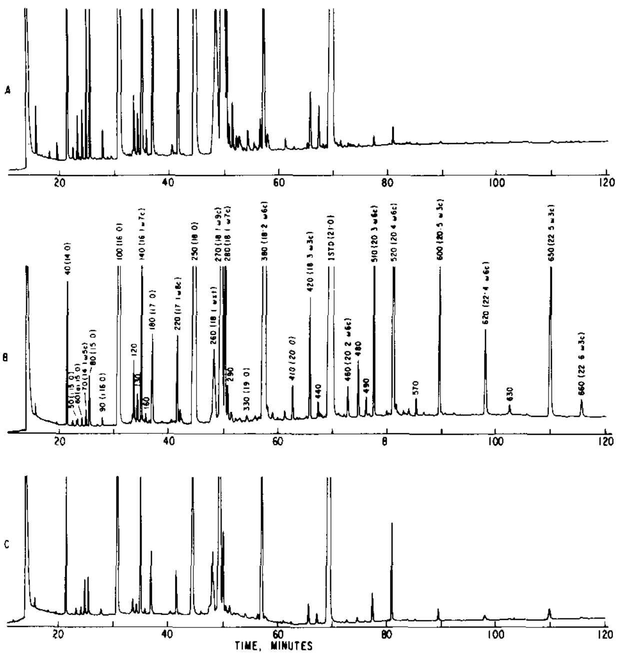

FIG. 2. Capillary gas chromatograms of neutral, polar and total fatty acid methyl esters (FAME) from bovine muscle tissue. A = neutral FAME, B = polar FAME, C = total FAME. Source: Ref (9).

TABLE VI

Composition of Animal Food Fats (wt %)[a]

Fatty acid	Beef	Chicken	Duck	Pork	Mutton	Turkey
10:0	–	–	–	0.1	–	–
12:0	0.9	0.1	–	0.2	–	–
14:0	3.7	0.9	0.7	1.3	3.8	0.9
16:0	24.9	21.6	24.7	23.8	21.5	20.6
16:1	4.2	5.7	4.0	2.7	2.3	6.0
18:0	18.9	6.0	7.8	13.5	19.5	6.2
18:1	36.0	37.3	44.2	41.2	37.6	35.9
18:2	3.1	19.5	12.0	10.2	5.5	21.2
18:3	0.6	1.0	1.0	1.0	2.3	1.4
20:1	–	–	1.1	1.0	–	–
20:4	–	0.1	–	–	–	0.3

[a]Agriculture Handbook 8-4, USDA.

rapidly. Only a few years ago, we were quite satisfied to determine the 10-15 principal fatty acids present in beef lipid with some precision. Recent publications, among them one by Maxwell and Marmer (9), demonstrate not only the advanced and sophisticated state-of-the-art of gas chromatography, but also illustrate the extreme complexity of the raw material that we simply call "tallow." In Figure 2, we have reproduced from Maxwell and Marmer's paper (9) the GC traces of fatty acid methyl esters obtained by transesterification of bovine muscle lipids. Trace C, the GC trace of methyl esters of the total lipid (neutral plus polar), shows only about 12 major peaks, representing 12 major fatty acid components, and merely hints at the multitude of minor components hidden in the baseline. Trace B shows the fatty acid methyl esters derived from the polar lipids, which themselves constitute only about 10% or less of the total lipids. It is apparent that many more components are present than could be labelled. Trace A shows the methyl esters derived from the neutral lipid portion of the fat. Altogether, there are perhaps 80-100 different fatty acids present in beef lipids, and about 70 of these have been identified with certainty. Assuming random distribution, the 80 or so fatty acids seen clearly on these traces could represent a total of over 500,000 triglycerides.

To the producer of fatty acids, such a detailed compositional analysis is of little importance. He is more likely to be interested in the gross composition of animal fats that may be part of his tallow and grease raw material, and more particularly, in the gross composition of beef fat (Table VI). Even analyses such as those shown here must not be taken literally, but should be considered illustrative only. The information that we can derive from this table is that oleic acid is the largest single component in all of these fats, that they all contain more palmitic than stearic acid, that linoleic acid is more plentiful in poultry fats, and that linolenic acid is uncommon. Meanwhile, it is also important to be aware that each sample of beef tallow or other animal fat will differ slightly in composition from the one that was analyzed yesterday, that the composition of the fat taken from any particular animal will differ, depending on the part of the carcass from which it is taken (10), and that when we are talking about the monoenoic acid 18:1, we are discussing a material that is predominantly oleic acid, but also may contain as much as 10-15% of positionally and/or stereochemically isomeric fatty acids.

Several studies indicate (7,8) that the composition of animal fats varies as a function of geographic location, breed, age, sex and feed of the animal. Many of these studies were carried out before gas liquid chromatography came into widespread use; however, more recent studies confirm the earlier findings (11,12). At any rate, in the production of fatty acids, most of these variables are fairly inconsequential, since the raw materials are normally composites of various sources, and therefore individual variations are minimized. One variable which does have some significance, especially in nonruminants, is feed and its seasonal changes in composition. This effect of feed can be seen particularly in pork fat, which varies considerably in hardness and in iodine value with the degree of unsaturation of the dietary fat (13). On the other hand, the hardness of beef fat is fairly independent of the degree of unsaturation of the feed, because of the ability of the rumen to hydrogenate polyunsaturated fatty acids to some extent. A variation in fatty acid chain length in beef fat as a function of feed variation also can be observed. The linoleic acid content of beef fat has been increased on an experimental basis by feeding beef a polyunsaturated oil, e.g., safflower oil, encapsulated in casein cross-linked with formaldehyde (14).

It has been mentioned above that the principal components of most fats and oils, including tallow, are triglycerides. These are converted to the free fatty acids or their soaps by methods such as fat splitting or saponification. It is helpful now to consider the animal sources of these fats and their further treatment to convert them to the tallows and greases of commerce.

Animal tissue containing fat is converted to tallow and grease by a process called rendering. Basically, rendering is a procedure by which lipid material is separated from meat tissue, bones and water by influence of heat. There are two principal methods by which this is done on an industrial scale. In the wet rendering process, the animal tissue is placed in an enclosed pressure vessel, and super-heated steam is injected to provide both heat and agitation. The mixture is cooked at 230-250 F for 3 to 6 hr. At the end of this period, the mixture settles into three phases: a top fat layer which is drawn off, an intermediate water layer, and a bottom phase consisting primarily of proteinaceous material. The dry rendering process was developed in the 1920s as a logical extension of the earlier "cook and press" kettle rendering procedure. Since the original animal tissue contains considerable amounts of water, and since it is the objective of the rendering process to separate the fat from the water and also from the bones and proteins, it was

TABLE VII

United States Renderers' Raw Materials/Production (1976) (16)

Source	Tallow and grease (Metric tons 000)	(%)
Beef	1532	42
Hogs	750	21
Lambs/sheep	19	NS
Poultry	258	7
Outdated consumer cuts	11	NS
Restaurant grease	718	20
Hide and trim fleshings	138	4
Dead stock	243	6
Totals	3669	100

TABLE VIII

United States Inedible Tallow and Grease (1983) (3)

Apparent production (thousand tons): 2595

	Disappearance (Thousand tons)	Percent	Percent of domestic use
Export	1318	50.8	–
Animal feed	636	24.5	49.8
Fatty acids	273	10.5	21.4
Soap	260	10.0	20.4
Lubricants/misc.	108	4.2	8.4
Totals	2595	100.0	100.0

logical not to add further amounts of water to the mixture. In the dry rendering process, then, the fatty tissue is heated in jacketed containers, mechanical agitation is provided, and the water is removed either at atmospheric or at reduced pressure as it is freed. Even more modern rendering plants feature a continuous rendering process, highly sophisticated air and water pollution prevention equipment, and automated operation. One such plant is capable of handling 3 million pounds of raw material each week (15).

Since the rendering process is primarily a physical separation procedure, and since relatively little refining is carried out on technical inedible fats, it is clear that the raw materials that the renderer uses to a large extent determine the composition of the product. There are well over 700 rendering plants in the United States, and for any one of these, the mix of raw material sources is likely to be a bit different from that of the others. In general, however, there are four principal sources from which the renderer obtains his raw materials: a) Packing house byproducts. These may contain adipose (subcutaneous fat), organ fats, offal, bones and even hide trimmings. b) Butcher shop trimmings. To a large extent, these are adipose and intermuscular fats, but they also include much bone, cartilage and outdated meat cuts–the latter often still in their polyethylene display packaging material. c) Restaurant grease. This can be quite varied in composition, depending on the type of food operation from which it originates. d) Fallen animals. In certain parts of the country, diseased and fallen animals present a disposal problem that is handled by the local renderer. In recent years, the "certified" tallow grade was introduced, primarily for the benefit of some foreign tallow buyers. "Certified tallow" is guaranteed not to contain fat from diseased or fallen animals.

We can gain a perspective of the relative importance of various rendering raw materials from figures published in the Spectrum (16), a yearly publication of the National Renderers Association (Table VII). While these figures are now eight years old, they seem to be the most recent ones published.

Given the variability of the raw material sources, it is not too surprising that there is a whole range of tallows and greases which differ not only in their degree of unsaturation, but also in the degree of abuse to which they have been exposed, either before or after rendering. In general, the hardness of a fat bears an inverse relationship to its amount of unsaturation. There are two reasons for this. One is that the unsaturated fatty acids, and hence their triglycerides, melt at lower temperatures than the saturated acids. The other reason is that the double bonds of unsaturated fatty acids represent vulnerable areas subject to chemical, and especially oxidative, attack.

It was mentioned above that besides triglycerides, animal

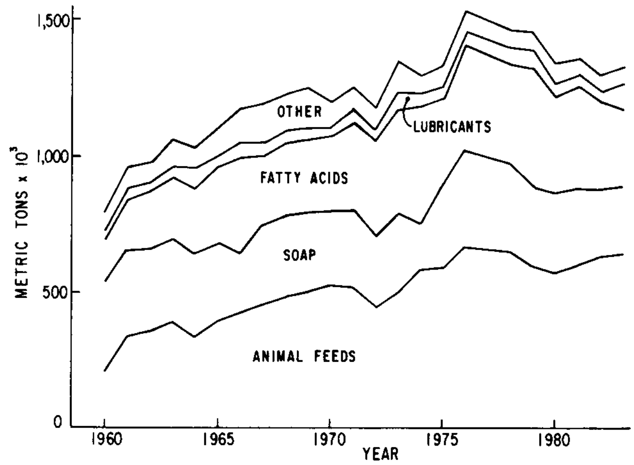

FIG. 3. Tallow and grease–nonfood uses in the United States, 1960-63.

fats also contain polar lipids. These are mostly phospholipids in which glycerol or the amino alcohol sphingosine is combined with a phosphoric acid residue and a base as well as with fatty acids. These types of compounds are normal cell wall constituents, and while they are present in relatively low concentration, their effect on the physical properties of the fat, particularly the surface properties, is substantial. Another group of compounds present in fats is usually classified under the term unsaponifiables, i.e., they are stable to and unchanged by potassium hydroxide in boiling ethanol. Among these are the sterols (particularly cholesterol), fatty alcohols, hydrocarbons such as squalene, carotenoids that have been introduced through the animal's feed, and others. The amount of unsaponifiables in tallow normally is in the 0.2-0.4% range. The free fatty acid content of tallow is one of the indicators used to establish grade. Free fatty acids in fats and oils occur as a result of hydrolysis, either chemical or enzymatic, of glycerides or polar lipids, and can be expected to be accompanied by a corresponding amount of mono- and diglycerides or lysophospholipids. Free fatty acids may range from <1% to 10-15%. Air oxidation of fats, particularly of their polyunsaturated fatty acids, results in the formation of hydroperoxides, which can be measured by titration. The hydroperoxides slowly degrade to alcohols, which together with ketones constitute further impurities that may be present and produce a characteristic rancid odor.

A discussion of animal fats as feedstocks for oleochemicals would not be complete without at least a brief overview of the relative amounts of these fats that are used in the various broad areas of application. From Table VIII, it can be seen that about one-half of the inedible tallow and grease produced in the United States in 1982 was exported. At home, by far the largest single use is in animal feeds, especially in formulated beef and poultry feeds and in pet foods. Generally, the less expensive grades of fats are used for this purpose, grades which are not particularly attractive to the producer of oleochemicals. Fatty acids and soaps consume about equal amounts of the higher grades of tallow. The 2.5:1:1 relationship between uses in feeds, fatty acids and soap has not always existed, as can be seen from Figure 3. The use of fats in feeds did not begin until the mid-1950s, after successful research sponsored by the Eastern Regional Research Center, USDA, and carried out at the laboratories of the American Meat Institute. At that time, the predominant use for tallow was in soap production. Since the late 1950s and early 1960s, petroleum-based detergents have taken over a large portion of the home laundry market, and uses of tallow in animal feeds and in fatty acid production have expanded constantly.

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