mean even smaller differentials in the future. Barring droughts or war, the problems of surplus disposal which we have increasingly faced in these past few years seem likely to continue unabated.

Industry Problems

The developments of the past and the prospects for the future emphasize the urgent need for solution of many problems in fats and oils. One in particular has attracted much attention in the past few years, and that is new uses for tallow and grease.

The struggle by the industry to find a solution to the "tallow problem" is, I believe, another good illustration of the relationship of economics and research and market development. It is a relationship which is stimulated and functions when prices are left to reflect true supply and demand conditions. With the accelerated loss of the soap market, tallow prices declined, and these lower and more attractive prices caused tallow to flow in increasing amounts into world trade. At a price all tallow produced in the past five years has found a market, though not a market which can be considered very satisfactory. But adjustments were made, which is in sharp contrast to developments in butter, cottonseed oil, and linseed oil. In these products high support prices have priced the products out of a large part of their market, increased government held stocks to mammoth proportions, and provided little incentive to the development of new uses and new markets.

But in tallow and grease, economic adjustments stimulated new and more vigorous research, and as a result tallow seems to be making a comeback. The problem is not solved, but there has been notable progress, and the most important from the standpoint of volume is the use of fats in feed. In little more than a year interest in and use of fats in feed have grown tremendously. The basic requirements were present in the known high caloric value of fats, and the need for correctives to the excessively dry and dusty condition of many feedstuffs, a condition incidentally, intensified by higher oil extraction from oilseeds through solvent processes, dictated in large measure by economic considerations. But the growth of fats in feed waited upon three principal factors: a) a price for fat that would make it competitive in cost with other feed ingredients; b) the development of stabilizers which would reduce or prevent rancidity in fat; and c) field tests to prove the favorable performance and economic worth of feed with added fat.

Coincident with the expansion of interest in the use of fats in feed, the prices of tallow and grease made a very appreciable recovery, and there was hope and fear, depending on one's point of view, that prices would go progressively higher as use in feed continued to grow. But there are two factors that work against this trend. First, of course, is the fact that the price of fats can soon reach a point where their continued use is uneconomic in relation to the cost of other feed ingredients. Secondly, and this illustrates the magnitude of the problem, to the extent that the domestic price structure strengthens, there is an almost inevitable opposing and moderating force in lessened export interest, an interest which could decline to zero as the domestic price approaches or surpasses world market prices for the same or competitive fats. When we consider that exports of tallow and grease alone amounted to nearly 1,200 million pounds in 1953, we have some measure of the magnitude of the tallow and grease surplus problem. Nevertheless the developing use of fats in feed is a very great step forward.

Other problems involve finding additional outlets for the expected continuing surplus of vegetable oils and vegetable oil foots. As the combined output of cottonseed and soybean oil continues to outstrip edible requirements, even more soybean oil will be available for industrial purposes. At the same time linseed oil will likely meet increasing difficulties as markets are lost to other oils and synthetic materials. The net price of vegetable oil foots has at times been below freight costs, in part a reflection of low tallow and grease values but more directly a result of high supplies and the loss of a large part of the soap market. The chief outlet for foots is in splitting, and further progress in the utilization of vegetable and of all fatty acids is a challenge for the future.

In thinking of the problems resulting from the invasion by synthetic materials into traditional fat and oil markets, we are faced with the fact that in the current chemical age this problem may become even more acute in the future. But tremendous technological gains have been made in fat processing in recent years, and more highly purified products with special capabilities have been and are being developed. As a result, the fats and oils industry is gradually getting in a position to wage a more vigorous competitive battle. The success of the battle will depend in large measure on how well we can meet and solve these present and future problems.

Vegetable Oils. Raw Materials for, and Recovery of, Inedible Fats and Fatty Acids[1]

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THE order of magnitude of the more important fats and oils in the United States is given in Table I. Those marked with an asterisk are the vegetable oils which are the subject matter of this paper while the others are given for comparison. The figures are for factory production, excepting palm, tung, babassu, and oiticica, which are for consumption since these oils are extensively imported. For the other oils the factory consumption is of the same order of magnitude as the production.

It is evident that soy, cottonseed, and linseed oils are the "big three" as to volume. However soy and cottonseed oils are used to a very great extent as edible oils and shortenings so their relative importance for inedible usage is not as great as these figures might indicate, but they are still of considerable importance. The same fact applies to corn and peanut oils whereas linseed, coconut, castor, palm, tung, oiticica, and safflower are used almost exclusively in inedible applications. Soy oil is used to a considerable extent in drying oil applications, particularly alkyds, while cottonseed and corn oils are little used as such in this field or for any other inedible use. However soy and cottonseed oils, and corn oil to a lesser amount, afford refining by-products, known as soapstocks which are the important raw materials for the production of vegetable fatty acids.

D. H. Wheeler

Fats and Oils, Raw Materials and Recovery

Soy oil. This is produced from the soybean by solvent extraction or by expellers. The use of expellers has been largely replaced by solvent-extraction, until today about 95% is by solvent extraction. Yield of oil is 15-20% of the bean. The general process of cracking the bean, tempering to proper moisture, flaking, and extracting the oil with hexane is well known and has been often described. The extracted meal is a valuable feed material. The crude oil left when solvent has been removed contains 2-4% of phosphatides or "lecithin" which will slowly precipitate on storage. This will interfere with many technical applications since it will cause darkening and precipitation when the oil is heated. The phosphatides are removed by hydration with 2-4% of water at moderate temperatures, which causes them to coagulate in such a form that they can be removed by centrifugation. The by-product lecithin is recovered and sold. The oil thus freed of lecithin is used in many industrial applications, such as soaps, blown oils, heat-bodied oils, alkyds, and modified oils. For many applications alkali refining with dilute caustic is used to produce a lighter-colored oil with very low acid value. Bleaching with active bleaching earths produces still lighter colored oils for special uses. Non-break soybean oil designates an oil from which the lecithin and gums have been removed so completely that it will not give appreciable precipitation of "break" material when heated in the standard break test with a trace of hydrochloric acid. Non-break oil may be made by alkali-refining of either crude oil or degummed oil. A very high percentage (about 80% or more) of crude soybean oil is refined, and the soapstocks produced as a by-product are an important source of raw materials for the production of fatty acids.

TABLE I
U. S. Factory Production
Oils and Fats, 1952

	Millions of Pounds	
	1952	1953
Lard, rendered	2,612	
Soy, crude	2,478*	2,515
Cottonseed, crude	1,717*	1,864
Tallow (ined.)	1,449	2,702
Grease	613	404 [1]
Linseed, raw	545*	493
Coconut, crude	435*	422
Tall, crude	312	318
Corn, crude	231*	259
Fish oils	120	130
Peanut, crude	101*	58
Castor, crude (1 and 3)	74*	50.7
[Dehydrated C. O.]	[16]	
Tung (production)	23*	41.5
Tung (consumption)	48	
Palm, crude (consumption)	33*	
Other vegetable crude (Incl. Palm kernel; Ref. Palm; rapeseed, olive, sesame.)	20*	28.6
Safflower	13	19
Oiticica (consumption)	10*	
Babassu (consumption)	8*	

[1] (Cons.)

The use of soybean oil in protective coatings is shown in Table II. The use listed as "Resins" largely reflects the increased use of soybean oil in drying alkyds, where the non-yellowing properties of the oil has led to greater usage in light-colored interior enamels and paints.

TABLE II
Factory Consumption of Soybean Oil in Drying Fields, Millions of Pounds

	Paint, Varnish and Protective Coatings	Resins	Total
1952	76.6	53.0	129.6
1951	64.2	64.0	128.2
1950	90.6	40.4	120.0
1949	94.2	31.6	125.8

Cottonseed oil. It is the next important oil as to total volume produced. However almost all of this oil is refined and used as an edible oil or in hydrogenated shortenings. Cottonseed oil is produced from the seed of the cotton plant as a by-product of the production of cotton fiber. In the past, production of oil from the cottonseed has been largely by hydraulic pressing or by use of expellers. More recently solvent-extraction has been used to give higher yields of oil. The meal is also a valuable feed material. Almost all of the crude oil is refined. The soapstocks thus produced are another main source of raw material for fatty acid production.

Linseed oil. This represents the largest volume of an oil produced primarily for inedible uses. It is the principal drying oil, used in outside paints, and in many interior protective coatings where color stability is not too important. Linseed oil is produced from the seed of the flax, grown domestically largely in the north central United States and parts of California. The method of extracting the oil was originally largely by pressing, with subsequent use of expellers, and more recently, solvent-extraction. Like most crude oils it requires some degree of refining to remove phosphatides, gums, waxes, and coloring matter. Prolonged storage of the crude oil in tanks has been used to cause "foots" to settle out and give a clear "break-free" oil. Addition of water speeds up the precipitation, and continuous processing with high speed centrifuges is the more modern method of removing foots from crude oil. A considerable amount of raw linseed oil is used by the paint industry. For many other applications, where a lower acid number or lighter color is desired, the oil is alkali-refined (batch or continuous centrifugal process) and bleached with bleaching earths and carbon. As before, the soapstock by-product is a source of fatty acids, but the quantities are much less than from soy and cottonseed oils. Acid

[1] Paper No. 171, Journal Series, General Mills Research Laboratories.

refining by treatment with sulfuric acid is also used to remove "foots" and coloring matter. Heat-bodied and blown linseed oils are also produced in considerable volume for use in protective coatings.

Coconut oil. It is the most important of the so-called lauric acid oils. The oil is recovered in about 60% yield from copra, which is the dried kernel lining of the coconut, fruit of the coconut palm tree. The tree grows in tropical climates, more recently by cultivation on plantations. The copra is usually produced at the location where the nut is harvested. The recovery of the oil from the copra is done largely in the countries using the oil, where the by-product cake is more valuable as livestock feed than it would be in the region which produced the copra. Coconut oil is used quite extensively as a minor constituent in solid soaps to impart foaming, and in liquid soaps and shampoos because of the solubility of the potassium soaps of coconut acids. The oil or fatty acid is used to make non-drying alkyds which are used as plasticizing resins with urea- and melamine-formaldehyde resins for white baking enamels. The alcohol corresponding to the acids is made by sodium or catalytic reduction of the oil, and then sulfated to produce a detergent. Much of the coconut oil is refined and used in special edible products, such as confections. Soapstock resulting from alkali-refining is used to make coconut fatty acids.

Babassu oil from the Brazilian palm and *palm kernel* oil from tropical oil palms are similar in composition to coconut oil and are similarly used.

Corn oil. This is produced from the germ of corn which is separated from the grain in the manufacture of corn starch. The germ contains 50-55% of oil which is recovered in the usual manner and refined to make salad and cooking oils. Very little is used for inedible purposes. The soapstocks from alkali-refining afford a minor supply of raw material for fatty acid manufacture. The same general situation also applies to peanut oil which is expelled and extracted from peanuts grown in the southern United States.

Castor oil. It is chemically in a class by itself in containing a major proportion (*ca.* 85%) of an unsaturated hydroxy acid, ricinoleic, 12-hydroxy, 9-octadecenoic acid. The oil is expressed or extracted from the bean of the castor plants, which are cultivated in tropical and sub-tropical climates, principally Brazil, East Africa, and India. The seed contains about 55% of oil, part of which is removed by cold pressing to give medicinal oil. The remaining oil is removed by hot pressing, expelling, or solvent-extraction. Because the meal is toxic, it is used only as fertilizer. Castor oil is used as a lubricant, in hydraulic fluids, and for sulfonation to produce turkey red oil, and as a plasticizer in lacquers.

Chemically, one of the most interesting uses of castor oil is for dehydration to dehydrated castor oil. Heating of the oil with acid catalysts eliminates water from the OH group on carbon 12 and a hydrogen on an adjacent carbon.

The dehydrated castor oil thus produced has a high content of 9,11 (conjugated) plus 9,12 (non-conjugated) diene groups. Some 30-40% of conjugated linoleate is present in unbodied dehydrated castor oil. The dehydrated oil as such, or after bodying to polymerize it, is a valuable drying oil used in making varnishes and alkyd resins for protective coatings. In 1952 some 16 million pounds of dehydrated castor oil was produced. Hydrogenation of castor oil produces 12-hydroxystearic acid (as glyceride), from which the acid is isolated and used as the soap in special greases.

Tung or *Chinawood oil* is another oil, which like linseed, is used almost exclusively in the drying oil field. It is unique in containing a high percentage (75-80%) of a fatty acid with three conjugated double bonds, eleostearic acid, or 9,11,13-octadecatrienoic acid. Recent work has shown that the 9-double bond is cis, and the 11- and 13-bonds are *trans* in the naturally occurring alpha eleostearate while the beta form is all-*trans.* The high content of a conjugated triene acid as glyceride makes the oil polymerize very rapidly by heat or autoxidation. It is therefore a useful drying oil for rapid-cooking varnishes and enamels. It gives films with excellent water and alkali resistance. It is also used to produce "crinkle" finishes due to peculiarities of volume change on drying. Spar varnishes are widely made from tung oil with phenolic resins.

Tung oil is produced by pressing or expelling the oil from the fruit. In the past China was the principal source of the oil, where it was expressed by very crude methods from fruit gathered from wild trees. The variable and often poor quality of oil thus produced, combined with world wars and political situations, has led to cultivation of the tree in many parts of the world, notably the U. S., Argentina, Paraguay and Brazil, although China still is the largest producer. In the United States its culture has been promoted by the government in a belt about 100 miles wide from eastern Texas along the Gulf of Mexico to the Atlantic Ocean. The peculiar demands of the tree as to rainfall and climatic conditions (long season, hot weather) limit it to this area. The increase in domestic production of tung oil over the past 10 years to 1952 is shown in Table III. It also shows the erratic pattern of imports and how consumption has followed the total available oil.

Palm oil. This is an oil imported into the United States from Africa and the Netherland East Indies where it is produced from the outer pulp of the oil palm from whose kernel the palm kernel oil is obtained. The oil varies greatly in fatty acid content (5-50%), depending on conditions of recovery. The oil is characterized by about equal parts of oleic and palmitic acids with minor amounts of stearic and linoleic acids. Its use in the United States is largely as a protective oil for tin baths in producing tin plate. It is also used for producing soaps and greases. Some of it is refined to produce oils used for edible purposes.

Oiticica oil, like linseed and tung oils, is used exclusively as a drying oil. It has a high percentage (*ca.* 80%) of a conjugated triene acid, licanic acid, which differs from eleostearic in having a keto group on carbon 4. It is used as a replacement for tung oil in varnishes. It is imported from Brazil, where it is obtained from the nut of the oiticica tree which grows in the north part of Brazil.

Safflower oil. It is a newcomer in the drying oil field. It has been produced as an edible oil in India and Europe, but only recently has it been produced from domestic seed in the United States. It is used as a drying oil, especially in non-yellowing alkyds and varnishes. Considerable work was necessary to develop species with suitably high oil content (*ca.* 30%) and yield per acre. It apparently is suited to

TABLE III
Tung Oil, U. S. Production, Consumption, and Import. Millions of Pounds

	Production	Consumption	Import
1942	2.3	11.8	8.3
43	5.3	12.0	.07
44	2.6	10.1	1.7
45	10.3	21.6	.34
46	11.0	28.9	32.2
47	12.7	88.4	121.5
48	16.8	120.8	133.5
49	22.4	100.8	64.9
50	23.4	98.2	112.8
51	12.6	65.0	29.7
52	23.1	47.8	29.8
53	41.5	47.7	

the great plains area, such as eastern Colorado and Wyoming, the Nebraska Panhandle, parts of Oregon, Washington and Idaho, and particularly the Imperial and San Joaquin valleys in California. Dollar yield per acre to the grower appears to be satisfactory, on suitable land, so the future increase of safflower culture will be interesting to follow. The seed may be processed by either expelling or solvent-extraction. The meal is apparently suitable for feeds but is lower in protein than soy or cottonseed meal unless the hulls are removed before extraction.

The oil is unusual in having the highest percentage of linoleic acid (70-80%) of any commercially available oil. Linolenic acid is virtually absent. It is therefore an excellent oil for non-yellowing alkyd resins as well as a somewhat slower acting replacement for linseed oil as a general drying oil, such as for making heat-bodied, and blown oils, limed oils, and varnishes. A catalytically conjugated safflower oil has recently been introduced as a replacement for dehydrated castor oil.

Fatty Acids, Materials, and Recovery

As mentioned above, the principal source of raw materials for inedible vegetable fatty acids is the soapstock produced in refining of vegetable oils. Cottonseed and soybean oils furnish the greatest volume of soapstock. Corn, coconut, linseed, and peanut oils furnish minor amounts of by-product raw materials for recovery of fatty acids.

The soapstocks are produced by alkali-refining of the crude or degummed oils. This may be done batchwise by stirring aqueous caustic with the oil and allowing the soap, with other impurities and with some entrained oil, to settle to the bottom of the tank. The refined oil is withdrawn, and the soapstock is recovered, containing about 50% water. It is acidulated with dilute sulfuric acid to produce acidulated soapstock. This is a mixture of free fatty acids, glycerides, and various other impurities. It is very dark and appropriately called "black grease." Instead of the batch-wise process, more modern practice is the use of continuous centrifugal refining. The aqueous alkali is mixed with the crude oil continuously by proportioning pumps. The soapstock is separated from the oil continuously by centrifuges. The centrifuge process leaves less neutral oil in the soapstock and thus gives a higher yield of refined oil. By the same token it makes the soapstock less desirable for the fatty acid manufacturer since the impurities are correspondingly increased in the soapstock. This factor and perhaps others have made cottonseed soapstock a more difficult raw material from which to make high quality fatty acids by distillation. Recent work has shown that cottonseed soapstock can be improved by a treatment with strong alkali. Whether the improvement given by such processes will justify their costs remains to be proved.

The figures for factory consumption of vegetable oil foots (100% fatty acid basis) and for the amount processed in splitting are shown in Table IV. The figures for the amount processed by splitting are a fair approximation of the amount used to make distilled and fractionally distilled fatty acids. Soy and cottonseed acids will constitute the majority of these soapstocks, but data are not available as to the relative amounts of each separately.

TABLE IV
Vegetable Oil Soapstock (100% F.A. Basis)
Millions of Pounds

Year	Factory Consumption	Processed in Fat Splitting
1949	200	134
50	213	147
51	163	101
52	193	143
53	190	—

Acidulated cottonseed or soybean soapstock, as now produced, is a mixture of free fatty acids, glycerides, coloring matter, sterols, other unsaponifiable matter, and oxidized acids.

Since the fatty acids which are present as glycerides would not be distillable, the acidulated soapstocks are hydrolyzed to release the fatty acids. This is done by repeated boiling with water and Twitchell reagent, or by a continuous high pressure, high temperature countercurrent splitting with water, usually without catalyst.

The split acids are then ready for vacuum-distillation. Simple distillation is done either in batch or continuous vacuum stills. Such a distillation removes a great deal of color in the polymeric undistillable residue. The distilled acids have a composition rather similar to that of the oil from which the soapstock was obtained. It can be bleached to a fairly light color. For some applications this composition is useful. For other applications (such as drying alkyds) the whole mixed acids (particularly cottonseed) contain too much saturated acids to be useful.

Several processes are used to remove the saturated acids from the unsaturated acids.

Low temperature crystallization from 95% methanol, or from acetone, is quite effective in removing saturated acids from cottonseed or soybean acids, and both operations are done commercially. The solution of fatty acids in solvent is crystallized in a continuous heat exchanger, and the crystalline slurry is fed to a continuous filter, where the cake of saturated fatty acids is washed with solvent and then fed to a still for removal of occluded solvent. The filtrate is similarly stripped of solvent to leave the unsaturated fatty acids as a residue. The process is also used to separate oleic acid from saturated acids of tallow.

Continuous fractional vacuum distillation is the other principal commercial method of removing saturated acids from cottonseed and soybean acids. The saturated acids present in these mixtures are mostly palmitic acid. Since palmitic acid boils about 17° lower than oleic and linoleic acids, it can be removed at the top of the fractionating still. A typical still would have three separate columns. The columns are operated under a vacuum as low as 2-3 mm., supplied by steam jet pumps. Multiple trays and bubble caps afford efficient fractionation. Heat is supplied by Dowtherm vapor in reboilers at the base of each column. Special molybdenum steel alloys are used to prevent corrosion.

The first column, fed continuously with split soapstock, removes moisture, low-boiling unsaponifiable matter, odorous constituents, low-boiling coloring matter, and some low-boiling fatty acids. The residue from this column is fed into the side of the second column, where the major fractionation by chain length occurs. A palmitic acid fraction is removed from the top of the second column. The main linoleic-oleic fraction may be taken off at a lower point in the second column, or the residue from the second column may be fed to the third column, where the linoleic-oleic fraction is taken off overhead. The final undistilled residue is withdrawn from the bottom of the third column and is further treated in a separate pitch still to produce pitch of required properties.

By thus removing the saturated acids from cottonseed acids by distillation or crystallization, the composition is changed from that of a slow or semi-drying oil (iodine value of 100 with 40-45% linoleic acid) to that of a drying oil (iodine value over 130 with 55 to 60% linoleic acid). Similarly, soy acids with iodine values over 140 with 60-65% linoleic and 5-8% linolenic acid, can be made. Very light-colored acids can be produced by fractional distillation.

These fractionated cottonseed and soy acids are used extensively for making air-drying and baking alkyd resins for use in protective coatings such as paints, enamels, and varnishes. The low linolenic count of soy acids, and its absence in fractionated cottonseed acids results in drying alkyds with a minimum of after-yellowing. This is especially desirable in white and light-colored enamels.

Fractional vacuum distillation is also used in fractionating coconut oil acids, which contain acids ranging from caproic and capric acids up to the 18 carbon acids. The principal acid is the lauric acid, which is readily obtained 90-95% pure.

Refractionation also affords the other component acids, capric, caprylic, and myristic acids, in equal purity.

Similarly stearic and palmitic acids over 90% pure are produced by fractional distillation of hydrogenated fractions of cottonseed and soy acids made from soapstocks.

Thus fractional distillation and crystallization of the fatty acids which are produced as by-products of vegetable oil refining now afford a series of fatty acids whose composition can be controlled to a considerable degree, compared to the mixture of acids which occur naturally as glycerides. This control of composition makes them of use as chemical starting materials for many applications where the unfractionated acids would be useless or less desirable. Where the natural composition of fatty acids is acceptable and the natural chemical combination with glycerol is desirable, the oils as such will maintain their useful place as raw materials for industrial uses. In uses where composition is important, and where the free acid affords more latitude or convenience in re-synthesis of new materials, fractionated acids will find an increasing field of use, particularly as new knowledge is gained as to the effect of composition to the properties and usefulness of fatty acids.

Recovery of Animal Fats

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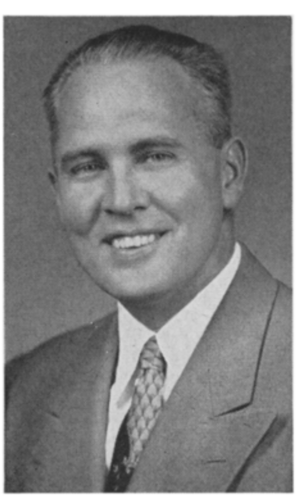
THE general field of fats and oils has developed technologically into a varied and viciously competitive one. It covers all of man's general classifications for matter, animal, vegetable, or mineral. The struggle for progress has been energized by human motivation of pleasure, profit, and more recently the desperate one of survival. The seriousness of the struggle for survival has been aggravated in some instances by the failure to recognize and practice some of the natural fundamentals that control the very existence of the industry.



Clark Rose

Any intelligent approach to the proper evaluation of optimum methods for producing animal fat products implicitly requires that the evaluation include the competitive position of the process not only within the animal fat industry, but also competitively to the corresponding mineral and vegetable products and processes.

The development of new frontiers in the production and utilization of animal fats must therefore never overlook these fundamental factors:

1. Animals not intended for edible uses cannot economically be produced solely as a source of fats. Therefore the recovery of animal fats is of necessity a by-product process. This is of extreme importance in the "survival" picture since it follows that low net production cost is of paramount importance.
2. As a compensating corollary, it follows that there will always be a "rendering" industry since inedibles must be disposed of. The nature of the disposal will be dictated by the economics of the best plan for such disposal.
3. As a by-product industry, the volume of raw material is relatively inflexible and measured only by the production and consumption of edible products. This seriously limits its end-use competitively with mineral or vegetable sources where supplies can be developed in line with demand.
4. In the animal by-products economy, the revenue from the recovery of fats is not necessarily the principal source of process revenue. At times other products may have the higher market value so that fat or oil may be in reality a by-product of a by-product. Fat may be 20% to 80% of the product revenue, and this fact serves definitely to limit the process selection since the specifications of the other products play a big part in the process economics. Proteins, minerals, biologicals, and other products have to be considered.
5. The various segments of the livestock, packing, canning, and merchandising elements of the meat industries all contribute their particular share of the raw materials supply, varying both in nature and quality. Raw material diversification is quite extensive.