

Processing for Industrial Fatty Acids - II

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ABSTRACT

Fatty acids are produced industrially from tallow, palm oil, palm stearin, palm kernel oil and coconut oil. The current and future supply situations of these raw materials and market economics favor palm stearin and palm kernel oil as major raw materials for fatty acids. The Malaysian oleochemical industry has adopted high-temperature and high-pressure "splitting" of triglycerides. Variations in product yields occurring in the processing of tallow and palm stearin and of coconut oil and palm kernel oil are indicated. Developments on the enzymic hydrolysis of triglycerides to fatty acids have been made, particularly in Japan. Enzymic hydrolysis at low temperature has the advantage of energy conservation compared to the high-temperature and pressure-splitting process. But enzymic hydrolysis is only applicable to triglycerides of low titre, such as palm kernel oil.

RAW MATERIALS FOR FATTY ACIDS

The major raw materials used for fatty acid manufacture are inedible tallow, crude palm oil, crude palm stearin, palm kernel oil, coconut oil, fatty acid distillate (deodorizer distillate) and acid oil. Other raw materials used to a lesser extent include rice bran oil, tall oil and rapeseed oil. The raw materials selected depend on the relative prices, availability and the specifications of the fatty acids required.

FUTURE TRENDS

Crude palm oil, palm kernel oil and crude palm stearin have become increasingly important as fatty acid raw materials.

Malaysia, the world's largest single producer of crude palm oil and palm kernel oil, produced approximately 3.1 million metric tons of crude palm oil and 0.3 million tons of palm kernel oil in 1983, which amounted to 54% and 45%, respectively, of the total world production of these oils. With a projected output of 6.5 million tons of crude palm oil and 0.7 million tons of palm kernel oil by the year 2000, these two oils are becoming increasingly competitive to tallow and coconut oil, respectively.

Fatty acids produced from vegetable-derived palm kernel oil and palm stearin if properly processed can be Halal and Kosher and are free of chick edema factor. These are important factors in food-grade fatty acids.

The United States is the world's largest single producer of tallow, a byproduct of the meat packing industry. Over the past years, tallow production has not increased significantly and is not expected to increase in future years. In 1983, the total world production of tallow was 6.0 million tons, while in 1979 it was 6.1 million tons. A direct consequence may be an escalation of tallow prices, favoring palm oil and palm stearin as replacements.

The total world production of coconut oil is projected to be 3.0 million tons by 1990. But, in spite of the larger supply of coconut oil compared to palm kernel oil, the prices of the latter are usually lower than those of coconut oil. This makes palm kernel oil an attractive raw material. Another factor favoring palm kernel oil includes its stable supply from Malaysia, due to predictable climate and better agronomic conditions.

RAW MATERIALS SPECIFICATIONS

Tables I, II and III show the accepted typical specifications for the fatty acid raw materials.

PROCESSING

Generally, the processing of oils into fatty acids involves pretreatment of the oils with phosphoric acid to remove phosphatides, followed by water washing to remove the residual acid. It may also be necessary to treat the oils with activated clay to remove heavy metals that may be present. For palm kernel oil and coconut oil, pretreatment is not necessary because these oils are relatively clean, whereas for crude palm oil, crude palm stearin and tallow, it is necessary that the oils be pretreated to remove impurities such as gums, soaps and solid matter. The type of pretreatment depends on the type and nature of the oils used. Pretreatment is also necessary to ensure that solid matter is removed from the oil. The pretreated oils are then split into fatty

TABLE I

Typical Specifications of Crude Palm Stearin Compared to Tallow

Specifications	Crude palm stearin (1)	Bleachable fancy tallow
Titre (C)	47 min.	40 min.
Slip melting point (C)	44 min.	—
Iodine value	32-36	40-56
Free fatty acid (%)	5 max.	5 max.
Moisture and impurities (%)	0.25 max.	—
Unsaponifiable matter (%)	0.80 max.	1.0 max.
Fatty acid composition (%)		
C12	0.1-0.6	—
C14	1.1-1.9	3.0
C14:1	—	0.5
C15	—	0.5
C16	47.2-73.8	25.0
C16:1	0.05-0.2	2.5
C17	—	1.5
C18	4.4-5.6	21.5
C18:1	15.6-37.0	42.0
C18:2	3.2-9.8	3.0
C18:3	0.1-0.6	—
C20	0.1-0.6	0.5

TABLE II

Typical Specifications of Palm Kernel Oil Compared to Coconut Oil

Specifications	Palm kernel oil (2)	Coconut oil (3)
Slip melting point (C)	25.9-28.0	20-24
Iodine value	16.2-19.2	7-12
Saponification value	243-249	250-264
Moisture and impurities (%)	0.5 max.	0.5 max.
Unsaponifiable matter (%)	0.1-0.8	1.0 max.
Fatty acid composition (%)		
C6	0.1-0.5	0-0.8
C8	3.4-5.9	7.8-9.5
C10	3.3-4.4	4.5-9.7
C12	46.3-51.1	44.1-51.3
C14	14.3-16.8	13.1-18.5
C16	6.5-8.9	7.5-10.5
C18	1.6-2.6	1.0-3.2
C18:1	13.2-16.4	5.0-8.2
C18:2	2.2-3.4	1.0-2.6
Others	tr-0.9	—

PROCESSING FOR INDUSTRIAL FATTY ACIDS

TABLE III

Typical Specifications of Raw Materials

Specifications	Rapeseed oil	Tall oil	Palm fatty acid distillate	Palm acid oil	Rice bran oil	Crude palm oil
Titre (C)	11- 15	16- 20			26- 30	40- 47
Iodine value	97-108	188-194			92-120	51- 55
Saponification value	168-180	125-136			184-195	190-202
Moisture and impurities (%)						0.5 max.
Unsaponifiable matter (%)			2.2-2.9		3-5	1.0 max.
Free fatty acid (%)			70 min.	50 min.		
Slip melting point (C)						
Total saponifiable matter (%)			95 min.	95 min.		
Fatty acid composition (%)						
C12						0.1
C12:1					0.5	
C14						1.0
C16	4.0	5.0			17.0	43.7
C16:1						0.1
C17	2.0					
C18		3.0			2.5	4.4
C18:1	19.0	46.0			45.5	39.0
C18:2	14.0	41.0			32.0	10.3
C18:3	8.0	3.0			1.0	T
C20		2.0			0.5	0.3
C20:1	13.0					
C22:1	40.0					
C24					1.0	

acids and sweetwater (15% glycerol) using demineralized water at 250 C-255 C and 50-55 bars pressure. This is almost the universal method of production of industrial fatty acids today.

Crude fatty acids emerging from the splitter may be processed into purer products with greater stability by hydrogenation, distillation or fractionation.

Fatty acids are hydrogenated at temperatures of 180 C-190 C and pressures of 20-25 bars to achieve an optimum reaction rate. The contact time between catalyst and fatty acids should be minimized to avoid formation of nickel soaps. Hydrogenated fatty acids are more stable to oxidation due to saturation of the double bonds. Therefore, the lower the iodine value the more stable the product.

Crude fatty acids are distilled or fractionated to yield products of acceptable odor, color, specification and stability. Most distillation plants are designed with facilities to take an odor cut or light end cut of 3 to 5% w/w of input, to separate the heavy fraction, as well as to remove residue. The acid value of the residue usually ranges from 30-50, and this can be adjusted by altering the distillation temperature.

In fractional distillation, fatty acids are separated into different fractions depending on feed composition, design of the fractionator (number of trays) and operating conditions such as feed temperature, reflux ratio and temperature, vacuum, etc. For separation of palmitic/stearic acids, a fractionator with a single column of 20 trays may be used. For separation of palm kernel fatty acids and coconut fatty acids into their fractions of C8/C10, C12, C14, C16/C18s', multi-columns are preferable.

Figure 1 illustrates the alternative processing with Routes 1, 2 and 3 to produce distilled hydrogenated fatty acids.

Route 1

This involves the distillation of the crude fatty acids followed by hydrogenation. This route produces fatty acids with a high nickel content which may cause a greenish color in the final product.

Distillation of the fatty acids prior to hydrogenation

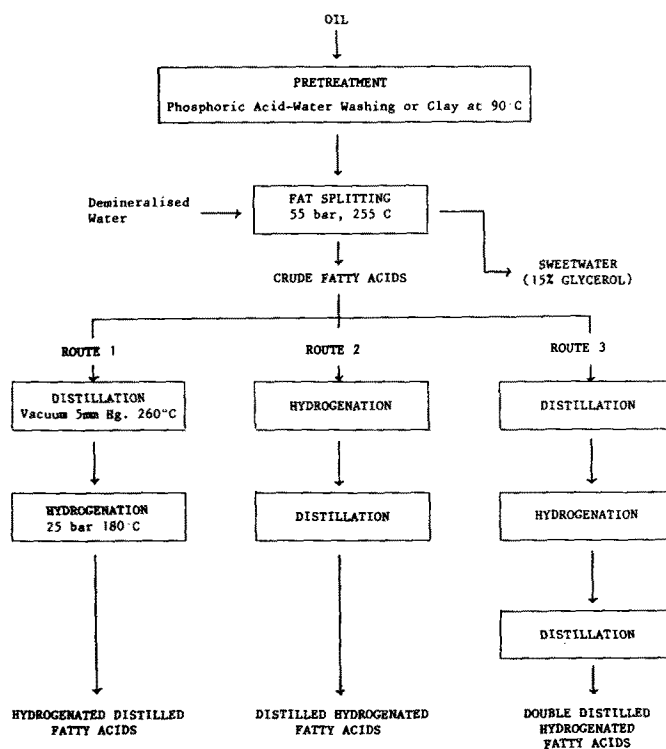


FIG. 1. Various process routes for the production of distilled hydrogenated fatty acids.

removes impurities and neutral oil so that only fatty acids are present to be hydrogenated. The catalyst is then less susceptible to poisoning. These two factors contribute to more effective hydrogenation and a reduction in nickel consumption.

Route 2

The crude fatty acids are first "hardened" by hydrogenation

followed by distillation. This route produces products of good color and color stability but the amount of nickel catalyst consumed is greater than Route 1.

Route 3

This route is similar to Route 1, but an extra distillation is conducted following hydrogenation. This second distillation removes the residual nickel catalyst in the product. This route is considered the best, resulting in products of good quality. However, the production cost is much higher than for Routes 1 and 2, and the overall distillation capacity of the plant is reduced.

In deciding which of the alternative routes to take in the processing of fatty acids, several factors have to be considered. These include the customers' specifications and the economics of the production cost compared to the cost of raw materials.

PALM STEARIN COMPARED TO TALLOW

The two main types of stearin available in the Malaysian market are hard and soft stearin. Hard stearin is normally available in the crude form and is produced by the wet fractionation of crude palm oil or by the Lipofrac process (by Alfa-Laval). Soft stearin is available only in the refined form as RBD (refined, bleached and deodorized) stearin, and is produced by the dry fractionation (Tirtiaux process) of RBD palm oil to yield RBD olein and RBD stearin.

It is estimated that Malaysia produced about 70,000 metric tons of crude stearin and 130,000 metric tons of RBD stearin in 1983.

Crude stearin, being a cheaper raw material than RBD stearin and crude palm oil, is becoming an increasingly important raw material to compete with tallow in the production of fatty acids in Malaysia today.

Table I compares the typical specifications of tallow and crude palm stearin. Palm stearin has a lower iodine value, less odor and is a cleaner material than tallow. The lower iodine value of palm stearin means a saving in hydrogen cost during hydrogenation of the fatty acids derived from it. Fatty acids from palm stearin can easily be hydrogenated to an iodine value of 1 using a catalyst dosage of nickel of below 0.08%, compared to a requirement of 0.25% of nickel for the hydrogenation of split tallow fatty acids to a similar iodine value. This means that palm stearin is a more economical source of palmitic and stearic acids than is tallow.

Using palm stearin for the production of fatty acids also results in a higher yield of product and less pitch. Table IV compares the typical yields of 90% palmitic acid and 90% stearic acid derived from hydrogenated tallow fatty acids and hydrogenated stearin fatty acids.

PALM KERNEL OIL COMPARED TO COCONUT OIL

Palm kernel oil and coconut oil have comparable specifications (Table II), and either may be used as a source of high-grade caprylic, capric, lauric and myristic acids.

There are no substantial differences in the processing of palm kernel and coconut oils, other than the yield differences of various products. A plant designed for fatty acid production from coconut oil is also suitable for the processing of palm kernel fatty acids.

The lower yield (7.5%) of the caprylic-capric blend from palm kernel oil is an advantage over that produced from coconut oil (15.5%) due to the limited market outlets of these acids. The yield differences of lauric acid and myristic acid derived from palm kernel oil and from coconut oil are only minimal (Table V).

Palm kernel oil produces stearic acid of 65-70% purity which resembles fatty acids derived from tallow, while coconut oil yields stearic acid of 55% purity.

OTHER ROUTES

Another approach to the production of fatty acids is enzymic hydrolysis. Lipase enzymes readily hydrolyze triglycerides. Currently, Japanese companies have plants of substantial capacity producing fatty acids by lipase hydrolysis of triglycerides. Several countries are also working on this biotechnological method of producing fatty acids.

Basically, the crude enzyme (10.0%) is added with agitation to a system containing the oil and water (1:1) at 30 C. Hydrolysis of the oil occurs slowly, and eventually the products fatty acids and glycerol are separated. This is facilitated by the addition of sulphuric acid (4).

This process consumes little energy and can produce light colored fatty acids. But a disadvantage of this process is the temperature limitation of 30 C, above which inactivation of the enzyme may occur.

QUALITY CONTROL OF RAW MATERIALS AND FATTY ACIDS

Raw Materials

To ensure that fatty acids produced conform to required specifications, it is important that the quality of the raw material is acceptable. Incoming raw materials are checked for the following specifications before unloading into the storage tanks:

1. FFA and M & I for crude palm oil, crude palm stearin
2. TSM, FFA for fatty acid distillate and acid oil
3. FFA, M & I and iodine value for palm kernel oil and coconut oil

Other specifications which are monitored regularly include unsaponifiable matter, chain length distribution and metal content.

Fatty Acids

During the processing of fatty acids, liquid samples are

TABLE IV

Comparison of Yields of Potential Palmitic Acids and Stearic Acids

From	90% min. palmitic acid (%)	90% min. stearic acid (%)	Residue (%)
Hydrogenated palm stearin fatty acids	60	32	8
Hydrogenated tallow fatty acids	28	57	15

TABLE V

Comparison of Yields of Fractionated Products from Hydrogenated Palm Kernel Fatty Acids and Hydrogenated Coconut Fatty Acids

Product	Hydrogenated palm kernel fatty acids (%)	Hydrogenated coconut fatty acids (%)
56% C8/C10	7.5	15.5
98% C12	46.5	46.5
95% C14	17.0	18.0
65% C18	24.0	—
55% C18	—	15.0
Residue	5.0	5.0

taken from the various plants at time intervals for analysis to assess the quality. The samples drawn at these stages are checked for iodine value, acid value or GLC, depending on the relevance of the data in relation to the desired product.

At the final stage prior to packaging samples are analyzed for the following: iodine value, titre, acid value, saponification value, unsaponifiable matter, color and FA by GLC. These specifications should conform to published standard specifications.

If the liquid sample is found to be out of specification, measures are taken to rectify the problem. The product may be redistilled to improve the color, for instance, or it may be blended with other fatty acids in a ratio that will meet the required chain length distribution.

When the liquid sample is within the desired specification, it is either bulked, flaked or drummed depending on the titre of the product. Regular monitoring of the heat color stability, ash content, moisture, impurities and nickel content, especially in the case of hydrogenated fatty acids, is important.

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Oleochemicals in the Plastics Industry

H. VERITY SMITH

ABSTRACT

There are opportunities for the producers of natural renewable products to manufacture downstream products of industrial value. The plastics industry is only one of many that offer such opportunities. Palm and coconut are two of the many plants with chemical possibilities.

INTRODUCTION

The northern industrial countries are in the process of transformation from "manufacturing" to "information" societies (1). As they pass from manufacturing economies to service economies (2) it will be the turn of the developing countries to become the industrial and manufacturing centers.

In order to render the transition into manufacturing societies as painless as possible, it is necessary that the developing countries concentrate on using their own natural and renewable resources. They should not follow the lines of development that were pursued in the northern industrial revolution, but should seek their own pathways, using their own resources and without relying upon organized assistance from the "old world." In its modern context, I take this expression to include Europe, North America and Japan.

As examples of new industrial enterprises for developing countries, based on renewable natural resources, it is proposed to consider the opportunities available to the producers of palm, palm kernel and coconut oils in the plastics industry. Similar opportunities exist in many other industries and are open to many other vegetable products in addition to those being studied at this conference.

It is suggested that petroleum must be replaced as the raw material of the chemical and plastics industry because supplies are about to be exhausted. The best estimates are that petroleum supplies will last into the third quarter (3) of the twenty-first century and natural gas into the last quarter (4).

It will indeed be argued that this is not the time for the developments I propose. There is presently a glut of petroleum on the world market, and in real terms, supplies are getting cheaper all the time (5). This is short-term thinking in a long-term context.

The best estimates suggest that, in real terms, petroleum (and therefore petrochemical) prices will start to rise in the mid 1990's (6). Such estimates cannot take into account escalation of the conflict in the Middle East. The programs

of development of products for the plastics industry which I am about to suggest could be coming to full fruition in about ten years' time.

REASONS FOR DEVELOPMENT

There are three reasons why downstream products from renewable vegetable resources should be developed now.

Commercial

In some cases, the oleochemical route produces a cheaper product under today's conditions. For example, linear alcohols are used in the plastics industry for the manufacture of stabilizers. At the average price of coconut and palm kernel oils over the last ten years, it has been cheaper to manufacture natural linear alcohols in the C₈-C₁₂ range than to make synthetic linear alcohols from ethylene by the Ziegler process.

World natural fatty alcohol production is about 260,000 tons per year, compared with about 420,000 tons of synthetic linear alcohols (7). The competitive position of the natural product will continue to improve with time, assuming that the vegetable oil producers keep up with the demand.

It is encouraging to observe the progress, both in the Philippines and in Malaysia, in the production of natural alcohols. There would appear to be no reason why the developing countries should not take over this market, providing that they remember that competition exists not only from synthetics, but from other natural products. It would not be the first time that a synthetic chemical had been ousted by a natural one. Synthetic glycerine is on its last legs.

Financial

There does not appear to be any sign that the banking community is making, or is likely to make, much contribution to the solution of the debt problem for which it is in large measure responsible (8). Currently, the third world is paying back more interest to the commercial banks than it is receiving in new financing (9).

Most developing countries must import all their petrochemical requirements, including plastics, and must pay for them in dollars. Most developing countries have a balance of payments problem and need to ration dollar foreign exchange. This has a delaying action on the industrial progress of developing countries because the necessary raw