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Processing for Industrial Fatty Acids - I

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ABSTRACT

Palm kernel and coconut oils are particularly important to the fatty acid industry because they are the major sources of lauric acid. This paper describes the processes used to convert these oils to their fatty acids. These in turn may be fractionated into saturated/unsaturated acids and to specific chain lengths by winterization, panning and pressing, fractional distillation, solvent crystallization and hydrophilization methods. The products are important raw materials for the soap, detergent and oleochemical industries.

INTRODUCTION

Palm oil, palm kernel oil and coconut oil are very significant parts of the economies of the ASEAN countries. These oils are also very important in the world's supply of vegetable oils. Coconut oil and palm kernel oil are particularly significant to the fatty acid industry and its customers, because they are the largest of a very few commercially available sources of lauric acid. Considerable research is being funded to find domestic sources of lauric acid in the largest consuming countries, but success of this research will not come before the AOCS meeting.

Let's look at the availability of coconut oil and palm kernel oil for the year 1983/84 (1) as presented in Table I. Coconut oil and palm kernel oil represent major raw materials for the manufacture of fatty acids and glycerine.

TABLE I

World Production of Major Vegetable Oils[1]

(1000 Tons)

	1983/1984 (Estimated)
Soybean Oil	13,361
Palm Oil	5,724
Sunflower Oil	5,703
Rapeseed Oil	5,279
Cotton Oil	3,056
Coconut Oil	2,387
Palm Kernel Oil	782
Total	36,292

[1]Source: *Oil World*

THE OILS

Table II shows that coconut and palm kernel oils have similar fatty acid chain length distribution. Both contain chain lengths from C_6 (caproic acid) to C_{18} saturated (stearic acid) and C_{18} unsaturated (oleic and linoleic acids). Both contain approximately 48% lauric acid. The major differences between the two oils are at the extremes of the chain length distribution. Coconut fatty acids have approximately 14.5% of the C_8 plus C_{10} fractions, compared to only 7.5% for the palm kernel oil fatty acids. The palm kernel acids contain 15% oleic acid versus 5% for the coconut fatty acids. These differences may lead to different desired processing steps to yield economically derived products for specific end-use applications.

TABLE II

Compositional Differences (%)

	Carbon Chain Length								
	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$
Coconut Oil	<1	7.5	7.0	48.0	16.5	8.0	4.0	5.0	2.5
Palm Kernel Oil	<1	4.0	3.5	48.0	15.5	8.0	2.0	15.0	2.5

HYDROLYSIS

The first important step in processing these oils is splitting or hydrolysis of the triglyceride to yield glycerine plus a mixture of fatty acids. The hydrolysis reaction can be done batchwise according to the Twitchell process (2) or continuously at high temperature and pressure using the Colgate-Emery process. This continuous countercurrent method takes from one to three hours to accomplish a 99% conversion. Today, almost all fatty acid manufacturers use the continuous process as shown in Figure 1. Also, of more recent interest is the enzymatic hydrolysis of triglycerides. Lipase enzymes from *Aspergillus niger, Candida rugosa* and *Rhizopus arrhizus* can be effectively used to split these oils; however, the enzymes are expensive and require longer reaction times (72 hours) to completely hydrolyze the oil (3). On the other hand, for comparison, Twitchell splitting may require 24 hours to realize an 85% split.

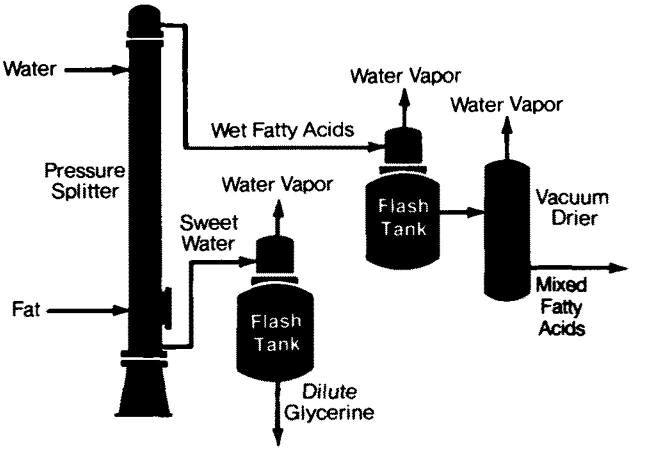

FIG. 1. The Colgate-Emery process of hydrolysis. Almost all fatty acid manufacturers use this continuous process today.

GLYCERINE

The glycerine obtained from the hydrolysis may be refined to a high purity (greater than 95%) by processing the sweet-

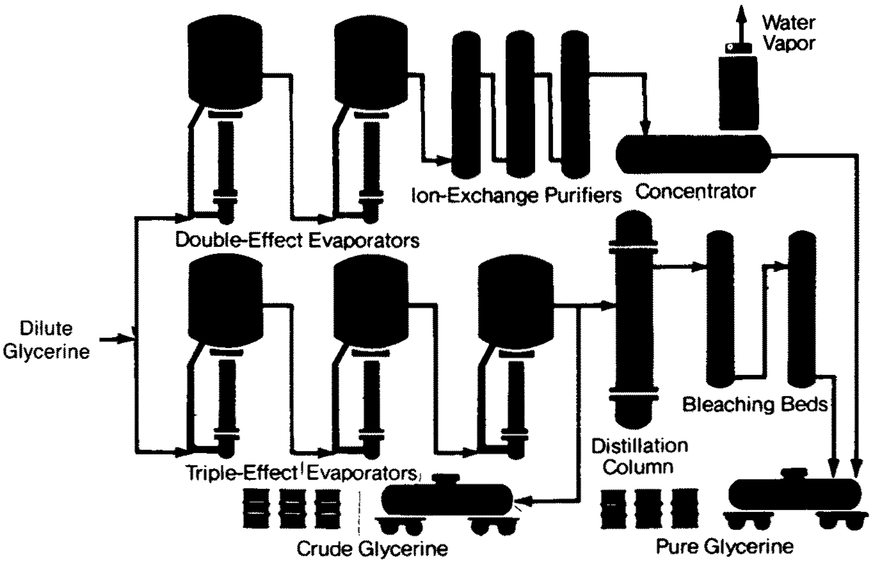

FIG. 2. **Glycerine refining by processing sweet-water through multiple effect evaporators, then distilling or deionizing.**

water through multiple effect evaporators, followed by distillation or deionization (4,5), as shown in Figure 2. Historically glycerine has been used by the cosmetic industry in lotions and creams to keep the skin soft and moist. It is also used in many personal care products such as shampoo, mouthwash and toothpaste, where it may function as a solubilizer and viscosity modifier. Glycerine is also used as a hemectant for the tobacco industry. Glycerine and many derivatives are used in chewing gum base, lubricants, triacetin, alkyd paints, cellophane, adhesives and soaps.

In addition, glycerine is used in the manufacture of polyether polyols, which are used in the production of polyurethane resins and urethane foams. Glycerine is also a byproduct of the methanolysis of these oils which will be discussed later. Since both oils are of vegetable origin the glycerine can be processed to a certified kosher product. The natural glycerine from these oils can be processed by multiple refining techniques to a very high (99.7% plus) purity product which is equivalent to, or purer than, glycerine derived synthetically. The refined natural glycerines also meet USP/NF requirements.

DISTILLATION

The split fatty acid mixture may be refined using distillation techniques. Distillation removes certain color bodies and odors which are indigenous to the oils or occasionally which have been caused by previous processing. Distilled products normally represent the first salable fatty acid products from the processing of the oils. The resulting distillation product typically retains the fatty acid chain length distribution found in the original oil. One of the largest uses of this "whole" fatty acid is in the manufacture of soaps and shampoos. The wide range of chain length distribution is desired for such soap properties as flash foaming and bubble size. These acids may also be reacted at the carboxyl group to yield esters, alkanolamides, etc., which find utility in many end use applications.

FRACTIONAL DISTILLATION

The mixture of fatty acids may be fractionally distilled to obtain individual fatty acids having purities in excess of 99% (6). Based on the compositions of the two oils, coconut oil would yield a larger quantity of C_8 caprylic acid and C_{10} capric acid. Many of these high-purity short-chain acids are reacted with mono- and polyhydric alcohols to make esters that are formulated into synthetic lubricants. The myristic and palmitic acids may be reacted with isopropyl alcohol to make the corresponding esters for use as emollients in cosmetic and personal care products. The lauric, myristic and palmitic acids may be converted to alcohols for use in detergent formulations. Fractional distillation will not efficiently separate the saturated C_{18} stearic acid from the unsaturated C_{18} oleic acid due to their boiling points and therefore, other separation techniques must be utilized (7).

SEPARATION

Presently three commercial methods are being used for separating saturated acids, such as stearic acid, from unsaturated acids, such as oleic and linoleic acids: winterization, the panning and pressing process and the solvent crystallization process. Under solvent crystallization four major commercial processes exist, including the Solexol process, the Armour-Texaco process, the Emersol process and the hydrophilization process. (8)

The earliest method of physical separation of fatty acids, dating back to the late 1800's, was called winterization or fractionation and effected a separation by the gradual cooling and crystallizing of the saturated acids. Many of the early separations using this method were done in the winter months only.

In the panning and pressing process, fatty acid mixtures are melted and poured into flat bottom pans and placed in a cool room to crystallize. The formed cakes are wrapped in cloth and placed in a press. Pressure is then applied to squeeze out the oleic acid while the stearic acid remains behind. This process was totally discontinued in the United States by the late 1970's.

The solvent crystallization process employs acetone (Armour-Texaco process) or methanol (Emersol process, shown in Figure 3) for solubilizing the fatty acid mixture. Upon cooling, the higher melting stearic acid crystallizes and is filtered from the fraction containing the oleic acid. The solvent is distilled from each fraction and recycled, while the resulting saturated and unsaturated acids are submitted to other refining operations. The Solexol process uses propane under pressure and the relative solubilities of the acids in propane to effect a separation. The single U.S.

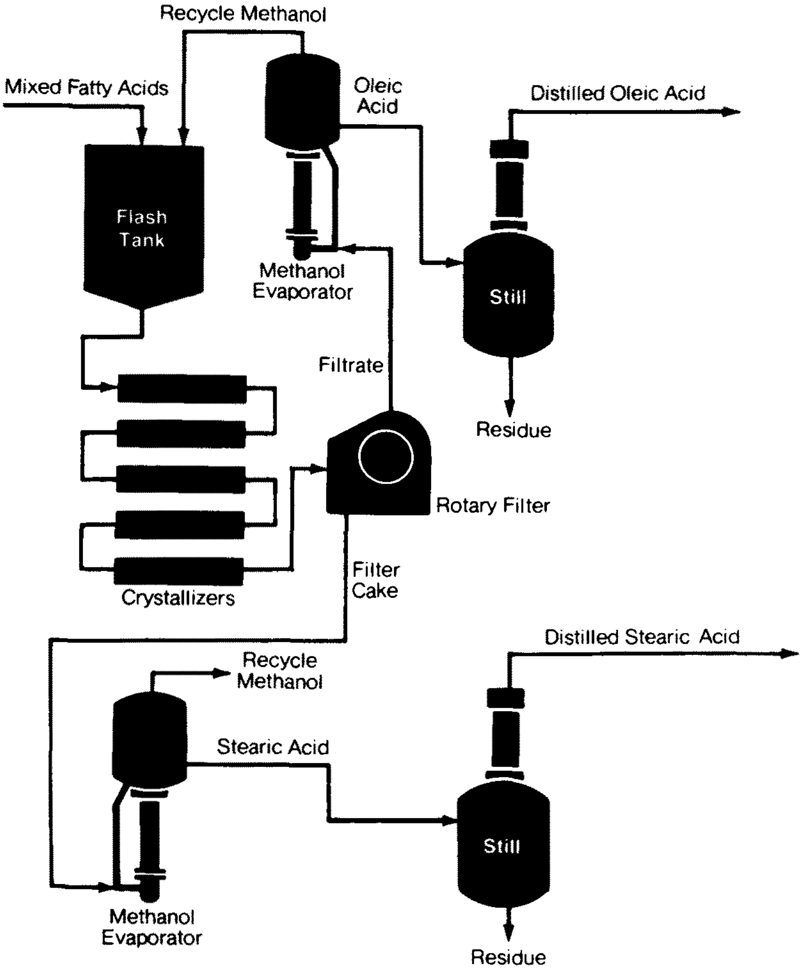

FIG. 3. The Emersol process of solvent crystallization.

plant built to use this technology was dismantled in the late 1960's.

In the past 15 years, all new separation plants built in North America by the fatty acid industry have been based upon the hydrophilization process. In this process, crystallized mixtures of fatty acids are contacted with a surfactant, thereby suspending the stearic acid in the aqueous phase which is separated from the oleic acid phase via centrifugation. This method of separation is not quite as efficient as the solvent crystallization process. For example, the iodine value of the saturated acid (16-25) is normally much higher than the iodine value (9-12) of the saturated fraction obtained from the solvent crystallization process. Because of this difference in efficiency between the two methods, hydrogenation of the solid acid fraction from the hydrophilization process yields a higher content stearic acid product and a lower yield of liquid acids.

Several newer methods of separation that are being investigated include: selective adsorption (9-11), air entrainment (12), transesterification-fractional distillation (13), methyl formate solvent process (14) and lithium soap separation (15).

Due to their low oleic acid content, coconut acids are not normally solvent separated but rather are distilled and fractionated. Palm kernel oil has a greater oleic acid content and therefore solvent separation may be of value. A combination of fractional distillation to remove the shorter chain length material (through C_{14}), followed by solvent separation of the palm kernel fatty acids could also be used to obtain oleic acid. This can be visualized from Table III, which shows the composition of the long-chain fatty acid cut.

One of the more common uses for oleic acid is in the manufacture of various soaps and detergents. Since water solubility increases with the degree of unsaturation, liquid sodium, potassium and triethanolamine soaps may be prepared from oleic acid. In many cases, oleic is combined with coconut or palm kernel fatty acids to provide differing desired foam structures and stabilities. Oleic acids are also used in alkyd epoxy resin esters and resinous polyhydric alcohol ester surface coatings, in cosmetics and toiletries as soaps, esters and emulsifiers, in textile chemicals as sulfated acids and esters, in pharmaceuticals as acid and polyoxyethylene sorbitan esters, and as plasticizers (alkyl oleates).

HYDROGENATION

Hydrogenation, also referred to as hardening, is used to convert unsaturated fatty acids to saturated fatty acids. The

TABLE III

Composition of Long Chain Acids in Palm Kernel Oil (After Fractionation)

C_{16}	29%
C_{18}	8%
$C_{18:1}$	54%
$C_{18:2}$	9%

oleic and linoleic acids present in both coconut and palm kernel fatty acids are typically converted to stearic acids, and the degree of hydrogenation is measured by the iodine value. Often, the fatty acids are refined by distillation prior to hydrogenation to remove sulfur contaminants and other materials detrimental to hydrogenation. The commercial hydrogenation of fatty acids has grown since the 1930's, when it was realized as an alternate approach to making a saturated product somewhat similar to the pressed or solvent separated acids. The main goal of hydrogenation is to lower the iodine value as quickly as possible. The efficiency of the catalyst and purity of the hydrogen are important factors in modern hydrogenation. Most fatty acids are hydrogenated in batch types of operation and utilize a catalyst such as nickel, platinum or palladium (16), with nickel being the most common and least expensive catalyst used in hydrogenation. Continuous hydrogenation of fatty acids is currently being practiced both in the United States and Europe.

Hydrogenation not only raises the melting point of the partially saturated fatty acid but also results in a more temperature-color stable product. Soap solubilities will, however, decrease as the actual saturated acid content increases.

End uses of stearic and palmitic acids include but are not limited to manufactured rubber goods and tires, buffing compounds, greases, metallic stearates, industrial soaps and textile specialties as well as candles, coated fillers for paper and plastics, and personal care products including soaps, shave creams, shampoos and cosmetics. Food grade acids function as lubricants in tableting, as well as raw materials for food grade emulsifiers and surfactants.

ALCOHOLYSIS

As mentioned earlier, the whole oils may be reacted with alcohols in the presence of an alkaline catalyst to yield fatty acid esters and released recoverable glycerine (Fig. 4). Methyl esters, which may be produced via the alcoholysis process or from the direct reaction of the acid and alcohol may be distilled, as is, or fractionally distilled to high purity esters. These methyl esters find use in the manufacture of alkanolamides for emulsifiers and detergents, shampoos and general purpose cleaners, and transesterification to higher esters, e.g., isopropyl myristate and palmitate. Other methyl esters, like methyl oleate, are used in the manufacture of antibiotics as a nutrient and defoamer. Methyl and ethyl esters can be used as diesel fuels or partial substitutes.

CONCLUSION

Each of the above-mentioned processes is designed to accomplish a specific end objective, and combinations of the processes are commonly used to generate desired products for specific end-use applications. With an understanding of each process, a fatty acid producer may opt for specific processes to most economically use coconut oil or palm kernel oil to produce the desired products.

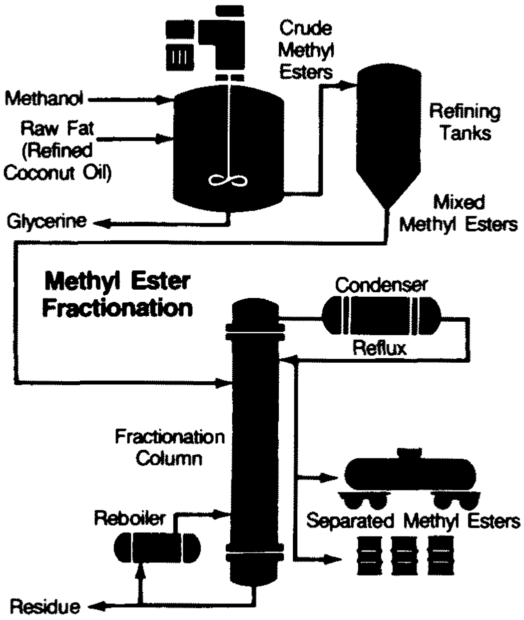

FIG. 4. Methanolysis

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