Separation of Saturated/Unsaturated Fatty Acids

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ABSTRACT

Fatty acid mixtures can be separated into one fraction rich in saturated fatty acids and the other rich in unsaturated acids. Since saturated fatty acids have a higher melting point than unsaturated, liquid mixture to be fractionated is cooled to a temperature at which the larger part of the saturated acids crystallize, while the greater part of unsaturated acids remain in liquid form. Different industrial methods to separate the two phases are described. The oldest and simplest method is slowly to cool and crystallize the mixture in shallow pans to form cakes which then are pressed in presses of different design. By applying high pressure, the liquid olein is thus squeezed out from the cake, leaving the stearin fraction behind. A new process to separate the phases is to mix an aqueous solution, containing a wetting agent, with the crystallized fatty acid mixture. The stearin crystals are thus wetted and transferred into the aqueous phase, which then can be separated from the olein phase in a centrifuge. The stearin/aqueous suspension is heated to melt the stearin, which can then be separated in a second centrifuge. Other methods to improve phase separation use organic solvents, among which are methanol, acetone, methyl formate and propane. In the solvent fraction process, the miscella has to be cooled to a lower temperature than in the aforementioned methods, due to the solubility effect of the solvents. The solvents are removed by distillation from the fraction. Typical operation results with different types of raw materials are given. The advantages and disadvantages of the different methods are discussed.

PRINCIPLES OF SEPARATION

Fatty acids are mixtures of different fatty acids, characterized by the carbon chain length and by the number of double bonds. A characteristic composition of fatty acids is specific for each kind of fat. The animal fats (e.g., tallow) consist of more than 50% saturated fatty acids, whereas some unsaturated vegetable oils, like soy and rapeseed, have less than 15% saturated acids. For most applications it is necessary to get this mixture separated into two fractions where one of them, often called "olein", contains the lowest possible amounts of saturated acids and the other one, called "stearin", contains the lowest possible amounts of unsaturated acids.

Basically, there are two principles which can be used to separate fatty acids from each other, both are based on specific properties. The vapor pressure varies significantly with the chain length and this is used to separate short- and long-chain fatty acids by means of fractional distillation. The vapor pressure does not, however, vary much with the degree of saturation.

On the other hand, the melting points of fatty acids change considerably with the degree of unsaturation, and this property is utilized in most of the industrial methods used today, for separating a mixture into saturated and unsaturated fractions. Sonntag and Zilch (1,2) reviewed the technical status in 1979 and also made a literature study on newer ideas, to improve the technique within this field.

A mixture of fatty acids is liquid at temperatures above the highest melting point of the individual acids in the mixture. By decreasing the temperature, the higher melting acids start to crystallize, as illustrated in Figure 1, where the simplest case is shown, e.g., where only two acids are present and where the two acids exhibit complete solid intersolubility. If we start from point A, representing a liquid mixture of the unsaturated acid U, and the saturated acid S, then decrease the temperature to point B at the liquidus curve, the first crystals formed will have a composition represented by point C. By decreasing the temperature further to point F, a mixture of a liquid represented by G and crystals with the composition C-H are formed. The composition of the fractions is influenced by the rate of cooling/crystallization. In practice, the crystallization mechanism is much more complicated due to the presence of more than two fatty acids and different kinds of impurities in the mixture, and also due to deviation from the supposed complete solid intersolubility and to the formation of mixed crystals (3-6).

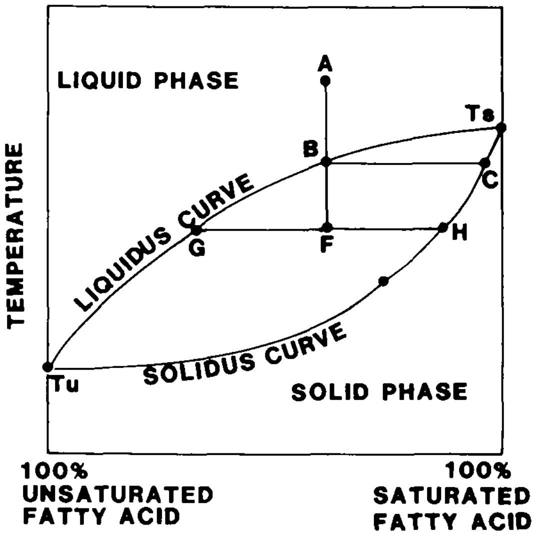

FIG. 1. Binary phase diagram for two fatty acids.

One conclusion to be drawn is that, in order to get pure fractions, repeated crystallizations and separations of the fractions must be done. Most industrial separation processes are based on the principle shown in Figure 1, although in certain processes the crystallization is done from a solvent miscella, which influences the phase diagram and therefore also the separation results.

PREPARING THE RAW MATERIAL

Independent of the process to be used for separation, it is important to define certain quality specifications of the feedstock. It is obvious that the content of mono-, di- and triglycerides, as well as other impurities, should be as low as possible, as otherwise these substances impair the results by remaining in either of the fractions (normally accumulated in the olein fraction). To get high quality products, it is also necessary to start from a crude stock with undamaged fatty acids, e.g., the acids should not be oxidized, isomerized, etc.

If the crude stock is derived from autoclave splitting of fats, a suitable precleaning before separation is often a straight distillation.

If the fatty acids from the soapstock are to be fractionated, a full saponification of the soapstock before splitting and then a bleaching or a straight distillation of the acid oil is recommended (7).

SEPARATION METHODS

Mechanical Pressing

This process, often referred to as "panning and pressing", is the oldest method and is basically very simple. It involves slow cooling/crystallization normally in shallow pans to a temperature where a solid cake has been formed. This cake is built up of a crystal network of high-melting fatty acids with the liquid, low-melting fatty acids filling out the space between the crystals. By applying high mechanical pressure, the liquid fraction, "olein", is squeezed out of the cake, leaving the remaining solid fraction, "stearin", behind.

The pressing can be done either batchwise in hydraulic presses at pressures up to ca. 200 bar or in continuously working presses, where the cakes are manually inserted between rotating filtering surfaces pressed against each other. This process has been practiced for many years with fairly good results, especially on fatty acids from tallow. The optimum crystal structure is attained when the saturated acids of the fatty acid mixture have a composition of ca. 55% palmitic acid and 45% stearic acid, and it is normally possible to get this proportion by blending different batches of animal fatty acids. Fatty acid mixutres from most vegetable origins do not have the above proportion of palmitic to stearic acid and are not so well suited to be separated by mechanical pressing.

A typical result by pressing tallow fatty acids is an iodine value (IV) of 10 in the stearin after one pressing, and down to IV 2 for a three-stage pressing. The olein phase has a titer in the range of 2-10 C.

The mechanical pressing is nowadays mainly used in older installations and at lower capacities; the main drawback is the high labor costs, as it is difficult to mechanize and automate the process.

The Hydrophilization Process

By using a water solution containing a wetting agent, it is possible to facilitate separation of olein and stearin. This opens the possibilty to automate the process. This process, which has been in commercial use for about 15 years, is sometimes called the Lanza process (8), the Henkel process (9) or the Lipofrac process (10).

The basic principle is simple and can be illustrated by a laboratory test. A partly crystallized mixture of fatty acids is mixed with a water solution of a wetting agent. After mixing, the slurry is centrifuged, and a phase separation occurs. The lightest fraction, i.e., the liquid fatty acids, is at the top of the centrifuge tube. Intermediate is a suspension of fat crystals in the water solution, and at the bottom is a more or less fat-free water solution. What has happened is that the fatty acid crystals are wetted by the water solution and are transferred from the liquid oil into the water solution, and when this has occurred, oil drops coalesce and the light oil phase can be separated from the heavy suspension of crystals in a water solution by means of centrifugal force.

The above-described laboratory test has successfully been developed into a continuous industrial process (Fig. 2). The crystal structure of fatty acids is comparatively simple compared to the structure of triglycerides and it is possible to cool and crystallize fatty acids rapidly for separation in the hydrophilization process. The melted fatty acids are pumped through a scraped surface heat exchanger, where the fatty acids are cooled and partially crystallized to a desired temperature by means of a suitable coolant, e.g., water or water-glycol solutions. The lower temperature limit is the freezing temperature of the aqueous wetting solution, e.g, ca. 0 C. The crystallized fatty acids are then mixed with the aqueous solution containing a wetting agent, which preferably is sodium decylsulfate, and an electrolyte as magnesium or sodium sulfate. The mixing is started in a small volume high-shear mixer to get a very intense mixing and disintegration of crystal clusters, then in a low-shear mixer with a larger volume where a "phase reversion" and coalescence occurs. The composition and the amount of the wetting aqueous solution are important parameters for optimum fractionation.

The dispersion formed in the mixers is separated in the first hermetic centrifugal separator. The light phase consists of the liquid fatty acids (olein), and the heavy phase is the stearin/detergent suspension. The olein is taken off to storage or for further treatment at this point.

The position of the interface zone between the light and heavy phases in the separator bowl is achieved by changing the difference between the pressures at the outlets.

After leaving the separator, the suspension is pumped through a regenerative heat exchanger, where it is preheated by hot recirculated detergent solution, then further heated to ca. 90 C by steam. The stearin crystals are thus melted and the emulsion formed is separated in a second centrifugal separator. The aqueous solution is recirculated to the process.

Table I shows some typical fractionation results by the hydrophilization process. It is possible to fractionate all kinds of fatty acids. The fractionation temperature is

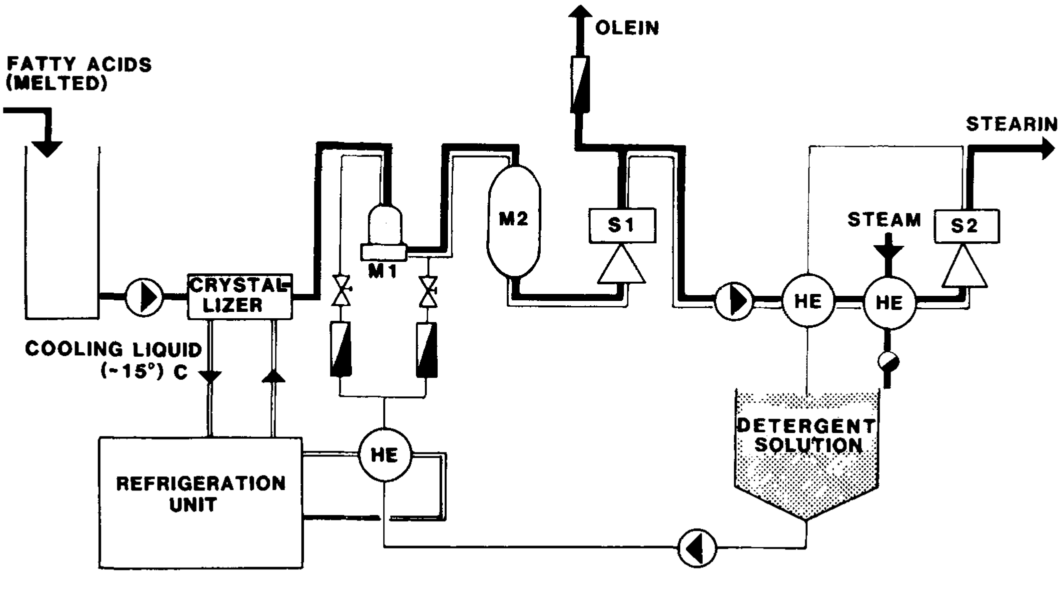

FIG. 2. Fractionation of fatty acids.

TABLE I

Fractionation of Fatty Acids by the Lipofrac Process

	Fractionation temperature (C)	Iodine value	Melting point (C)	Yield (%)
Tallow FA	12	53	42	
Olein		96		53
Stearin		22	51	47
Palm oil FA	15	57	41	
Olein		103	10	44
Stearin		23	49	56
Tall oil FA	5	143	27	
Olein		164	a	77
Stearin		63	50	23
Soy oil FA	2	136		
Olein		154	b	78
Stearin		78		22

[a] CP = Cloud point = -5 C.
[b] Content of saturated FA = 3.5%.

dependable on the composition of the fatty acids. In Table II is shown the influence of the fractionation temperature, where the feedstock was a mixture of fatty acids from some vegetable oils with IV of the mixture of 98. The lowest IV in the stearin was obtained at the highest fractionation temperature (22 C), but at this temperature the olein phase still had much saturated fatty acids in solution. By decreasing the temperature to 10 C and further to 7 C the yield of olein decreased, whereas the iodine value of the olein increased and the cloud point and titer decreased. It is possible to get better overall separation of the saturated and unsaturated acids by a two-stage fractionation, e.g., by making the first fractionation at 20-25 C and then a second fractionation of the olein phase at 2-3 C.

Synthetic fatty acids with IV 35 and containing 11% unsaponifiable matter gave, after fractionation at 44 C, 65% olein and 35% stearin. The olein had IV 45 and contained 15% unsaponifiable matter, whereas the stearin had IV 15, a melting point of 62 C and only 3.5% of unsaponifiable matter. This is an example of the general rule of crystallization that impurities are accumulated in the mother liquor, e.g., the olein.

Figure 3 shows the distribution of the fatty acids from palm oil between the two fractions.

Typical utility consumption figures for a hydrophilization process are shown in Table III.

Fractional Crystallization from Solvents

Solvent processes utilizing liquid to liquid countercurrent extraction have been developed and used for fractionation and also for refining of fatty oils and fatty acids. Solvents which have been used are furfural and liquid propane. The latter solvent is used in the so-called Solexol process.

However, the more important processes utilizing organic solvents involve separation methods by crystallization of saturated fatty acids from a solvent solution of a fatty acid mixture. Several solvents, mainly of the polar type, have been used and the most commercially successful one is methanol in the Emersol process (Fig. 4).

Fatty acids are dissolved in 90% methanol to yield ca. 30% concentration. The solution is then pumped through a series of precoolers and coolers/crystallizers down to ca. -15 C. The crystallizers are multitubular units equipped with scrapers for improved heat transfer and circulating methanol is normally used as coolant. The slurry of crystallized fatty acids in the mother liquor flows to a rotary vacuum filter. The filter cake is continuously washed with fresh solvent to remove mother liquor. To prevent clogging of the filter cloth, this is washed by hot solvent.

TABLE II

Influence of Fractionation Temperature in Lipofrac Process

Fractionation temperature (C)	Olein IV	Olein Cloud point (C)	Olein Titer (C)	Olein Yield (%)	Stearin IV	Stearin Yield (%)
22	101	18	19	78	23	22
10	122	4,2	8	67	26	33
7	132	0,4	4	59	44	41

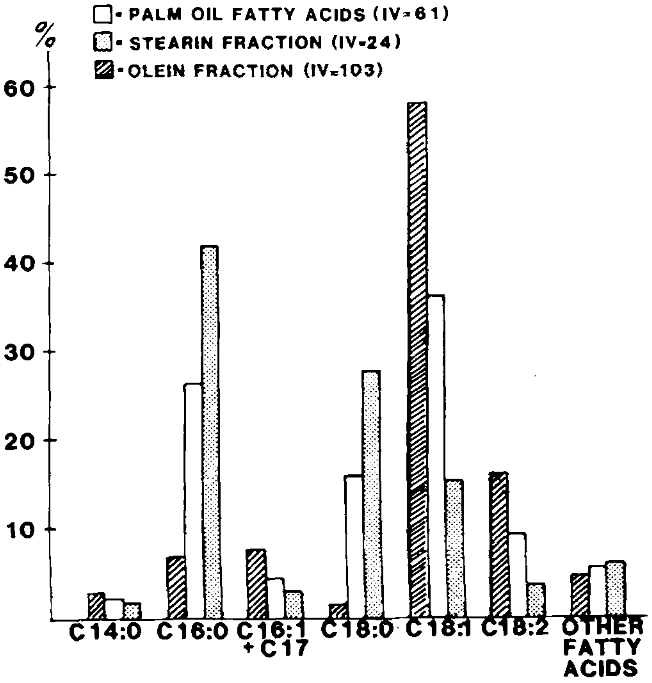

FIG. 3. Fatty acid composition of olein and stearin fractions from palm oil.

TABLE III

Utilities Consumption in Lipofrac Process per ton of Fatty Acids

Steam (120 C)	170 kg
Process water	0.2 m^3
Cooling water (recirculation)	1 m^3
Electrical energy	34 kWhr
Sodium decyl sulfate	2-5 kg
Sodium sulfate	1-2 kg
Instrument air	5 nm^3/hr

The filter cake, containing ca. 50% methanol, is melted and stripped of solvent, which is returned to storage. The mother liquor is likewise fed into a stripper for recovery and recycling of the alcohol.

Typical fractions obtained in the Emersol process from tallow fatty acids are: the stearin fraction with IV 8 and titer 54 C; the olein fraction with IV 93 and titer 3 C. From soybean fatty acids is produced a stearin fraction (mainly palmitic acid) with IV 50 and titer 49 C; and an olein fraction (mainly linoleic acid) with IV 144 and titer 3 C.

The so-called Armour-Texaco process is similar to the Emersol process and gives similar results, but in this process a hydrous acetone is used as solvent. Other solvents suggested and patented for fatty acid separation are hexane, methyl ethyl ketone and methyl formate.

TABLE IV

Comparison of Fractionation Processes

	Mechanical pressing	Hydrophilization process	Fractional crystallization from solvents
Merits	Simple	Works on most kinds of FA	Works on most kinds of FA
	Low investment costs	Low operation costs	Highly automated
	Good stearin quality	Good olein quality	Good stearin quality
Drawbacks	High operation costs	High investment costs for small capacities	High investment costs
	Restricted to mainly animal fats		High operation costs (energy solvent loss)
	Messy		

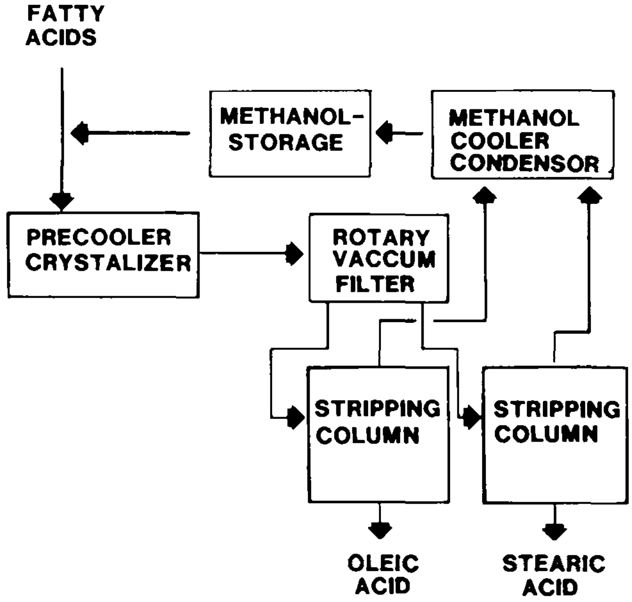

FIG. 4. The Emersol process (simplified flowchart).

COMPARISON OF SEPARATION METHODS

Each of the above described processes has its advantages and drawbacks. In Table IV, an attempt is made to summarize these subjectively and qualitatively.

Only under special conditions can the mechanical pressing plants compete nowadays, and very few plants of this kind can be expected to be built in the future. The main problems are high labor costs and comparatively bad working conditions for the operators.

By comparing the two remaining processes, it can be stated that the hydrophilization process is superior in producing a high-quality olein, whereas the solvent methods produce a somewhat better stearin. For many applications, the stearin must have an IV lower than can be produced by any of these processes. In such cases, the stearin fraction is often hydrogenated to IV 2 or below.

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