The Hydrophilization Process for the Separation of Fatty Materials[1]

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Abstract

Fats and derivatives of fats consist of mixtures of components differing in chain length and saturation. Apart from the fractional distillation, several methods exist for the separation which are based on the different melting-point and solubility behavior of these components. Modern separation processes use recrystallization from organic solvents, press or filtration methods. The hydrophil process uses an entirely different approach. A mixture of solid and liquid fatty material, for instance, tallow fatty acid, is treated with an aqueous solution of surface-active substances. The liquid fatty acids are removed from the surface of the fatty acid crystals and emulsified in the aqueous phase. The crystals are hydrophilized so that they leave the oil phase and completely enter the aqueous phase, where they are suspended. In a solid-bowl centrifuge the aqueous solution, containing the suspended crystals of stearic acid, is separated from the oleic acid phase. The stearic acid is recovered by heating the aqueous suspension above the melting point.

The composition and concentration of the surfactants, the salt content and the volume of the aqueous phase, the crystallization performance of the fatty material, and the apparatus design are important in the efficiency of the separation. The composition of the components is based on the phase diagram which controls iodine number, melting or cloud point of the oleic and stearic acid in relation to the separation temperature. The stearic and oleic acid is practically identical with the expected composition from the phase-diagram readings. This separation principle can be used for fatty acids, fatty alcohols, or fats.

Introduction

NATURAL FATS and their derivatives, such as fatty acids, fatty alcohols, etc., consist of compounds differing in chain length and saturation. Since the characteristics of such products largely depend on these properties, fractionation methods have recently met with growing interest. Processes based on the separation of fatty material into saturated and unsaturated components (solid and liquid phases) have been known for a long time. The principle of crystallization is applied in conjunction with various filtration methods. For many years hydraulic presses have been used for obtaining stearin and olein. Recent processes apply the method of crystallization from organic solvents. Both processing techniques have disadvantages. These consist mainly in the poor filterability of fatty material, in a high expenditure of work, or in measures necessitated by the use of organic solvents.

Experimental Procedures

This laboratory has devised a process which is based on a completely different principle of separation. The mixture of solid and liquid components which is to be separated (to simplify matters the following will mainly deal with fatty acids) is treated with an aqueous solution of surface-active agents. As a result of the wetting effect of these solutions the liquid components are detached from the surface of the solid components and emulsified in the aqueous phase. By this treatment the crystal surfaces are wetted with water so that the solid fatty acids move into the aqueous phase, where they are suspended. One gets a dispersion in which the liquid fatty acids are emulsified and the solid fatty acids are suspended in water.

Fig. 1 (left side) shows a microscopic photo of such a dispersion. One will recognize the oil drops emulsified in the aqueous phase and the suspended crystals. Further, one sees that the oil no longer contains any crystalline components and that no oil sticks to the suspended crystals. About 60 years ago similar tests were also made by Twitchell (2). However there was no workable method of decomposing such dispersions. If they are centrifuged, however, there is separation into layers in which the liquid fatty acids are the top layer. Below is the aqueous phase, in the upper part of which the crystals are situated. The separation of phases is exeremely sharp. The oil is completely separated from the aqueous phase and free from crystals. Without the use of surfactants one gets no separation. It is also obvious that separation is impossible without using the aqueous phase.

By wetting the crystals, the surface activity of the aqueous phase is effective in that crystals are forced into the aqueous phase contrary to their relative density. This renders the layer of stearin crystals very solid. If however the separation of phases is carried out continuously in a solid-bowl centrifuge, the stearin suspension remains easy-flowing and the dispersion can be separated quite simply (Fig. 1, right side). The two liquid phases, the oily and the aqueous stearic slurry, are removed separately. The liquid fat or fatty acids are separated from the suspended stearic completely. Stearin is obtained from the aqueous phase after melting. The fundamental advantage of this method of separation lies in the fact that no solvents are used and that the solid-liquid separation which necessitates a pressing or filtration step is changed into a liquid-liquid separation. Thus all problems involved with the filtration of fatty material are eliminated.

The flow sheet of the separation process is shown in Fig. 2. The fatty acid is pumped in the molten state from a storage tank through the cooling system by means of a proportioning pump. The slurry mixture of liquid fatty acids and solid fatty acid crystals, which develops by crystallization, enters into a mixer, where the oil components are detached from the crystal surfaces. For that purpose a concentrated solution of the wetting agent is put in this mixer with a metering pump. The developing dispersion is diluted in steps by the returned aqueous phase of the process. Subsequently the dispersion flows through the centrifuge, where the oleic acid and the suspension of stearic acid in the aqueous phase are separated. In a heat exchanger this suspension is heated above the melting point of stearic. Then the molten stearic

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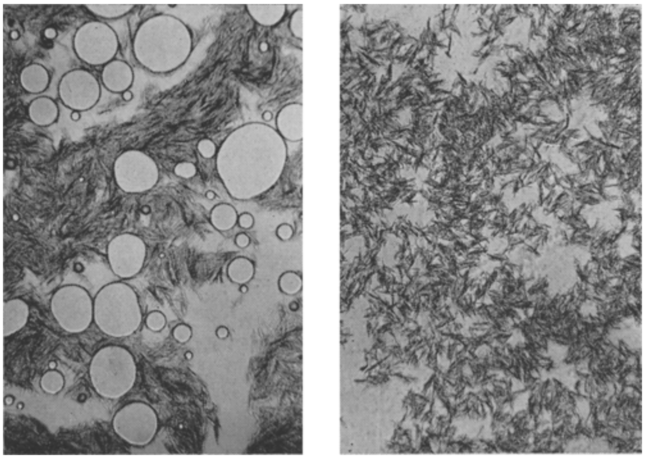

FIG. 1. Microscopic photo of the dispersion *(left)*. Microscopic photo of the stearic slurry *(right)*.

is separated and washed like the oleic; after cooling, the aqueous phase is returned to the separation process. Part of the surfactant is recycled with the water. The amount of wetting agent in the stearic before washing is approximately 0.2%. Owing to adsorption on the surfaces of the solids, the content is higher than in the oleic with 0.02%. There are no difficulties with washing.

Discussion

With regard to the individual processing conditions, crystallization is, of course, an essential part of the process. The crystallization characteristics of the fatty material to be separated have to be taken into account. The separation process does not change anything in these characteristics. Generally, fatty acids crystallize so easily that crystallization in cooling systems with rotating scrapers is satisfactory in about an hour. If the amount of solids in the products to be separated is so small that the product remains easy-flowing after crystallization, cooling may also be done discontinuously. Fats and fatty alcohols usually need more time for crystallization, which may be brought about by repeated passing through scraper-coolers. Often crystallization of fatty material can also be carried out in the presence of the aqueous phase. The dispersion develops while the fatty material cools, and subsequently separation is effected in a solid-bowl centrifuge.

A great number of surfactants have proved to be appropriate. Satisfactory results are obtained with fatty alcohol sulfates or alkyl benzene sulfonates, but soaps, alkane sulfonates, cationics, and nonionics also are appropriate. It is quite obvious that the complete separation of liquid fatty acids depends not only on the chemical composition of the wetting agent but also on other factors such as its concentration, the salt content, and the quantity of aqueous phase. A content of 1–2% of an inorganic salt in solution in the aqueous phase has proved to be advantageous to the process. Generally $MgSO_4$ is preferred in this laboratory.

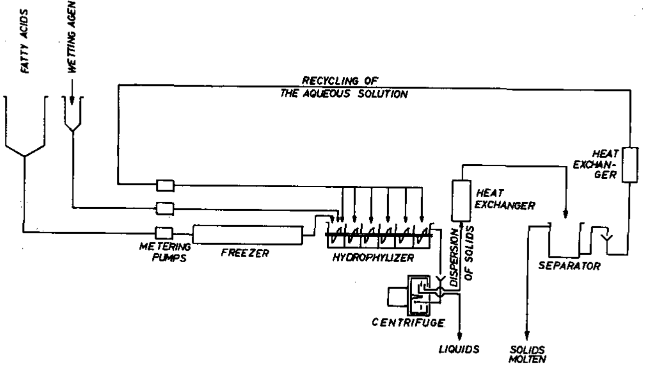

FIG. 2. Flow-sheet of the hydrophilic separation process.

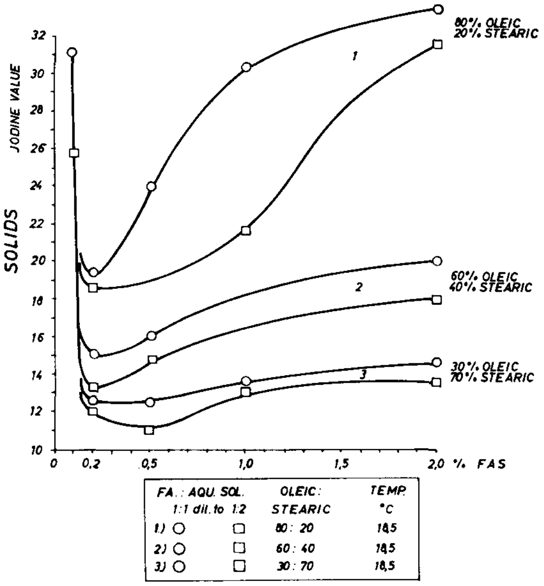

FIG. 3. Iodine value of the stearic vs. wetting-agent concentration.

Fig. 3 illustrates the dependence of the iodine number of the stearic on the concentration of fatty alcohol sulfate. The diagram shows the values obtained by using a quantity of aqueous phase corresponding to the quantity of oily phase, also the results which are reached when the aqueous phase is diluted to twice this quantity. One sees that a stepwise dilution gives a better separation. This observation is generally applicable. The dispersion should be produced so as first to bring together the crystalline fatty acid with the wetting agent in higher concentration and then to dilute the dispersion in steps. Further, with increasing concentration of the wetting agent, the degree of separation passes an optimum. The separation of liquid fatty acids is incomplete with too little as well as too much wetting

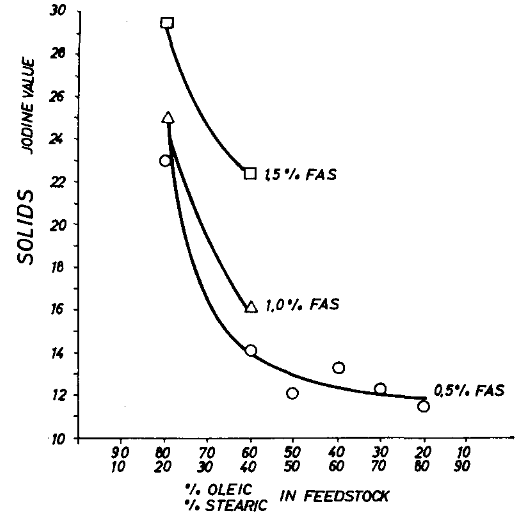

FIG. 4. Iodine value of the stearic vs. stearic-oleic ratio.

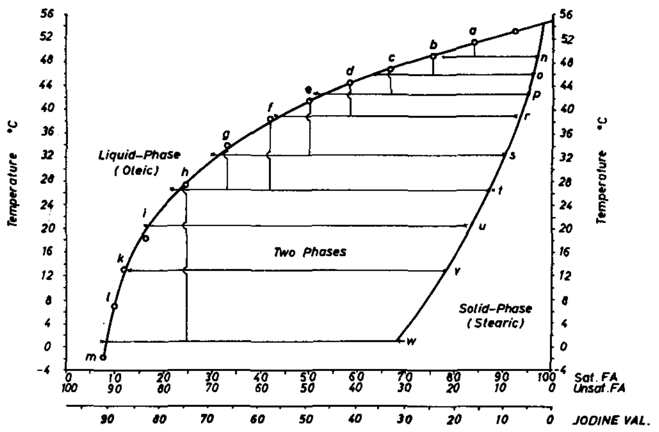

FIG. 5. Phase diagram of tallow fatty acid.

agent. However the optimal range is so large that dosage presents no difficulties.

The diagram further shows that the iodine number of the stearic also depends on the quantitative ratio between oleic and stearic in the fatty acid which is fed in. The higher the proportion of stearic, the lower the iodine number of the stearic obtained. It does not depend on a more or less complete oil separation but is based on the crystallization behavior (Fig. 4). The stearic acid crystallizing from a solution of stearic acid in oleic acid is not pure. These ratios can be shown in a phase diagram between oleic acid and stearic acid.

Fig. 5 shows such a diagram for mixtures of technical oleic and technical stearic as they occur in tallow fatty acids. It represents the relation between the composition of oleic and stearic and the temperature in the state of equilibrium. The upper curve describes the oleic composition and the lower, the stearic composition, depending on the crystallization temperature. If molten tallow fatty acid, which contains almost the same amounts of stearic and oleic, is allowed to cool down, crystallization takes place at the temperature related to Point e). The oleic composition is the one corresponding to Point e). The precipitated stearic has a composition corresponding to p). Further cooling leads to increased crystallization. The composition of oleic follows the Curve e/m), and that of stearic follows the Curve n/w).

The higher the proportion of stearic in the original material, the lower is the iodine number of the precipitated stearic. The higher the separation temperature chosen, the lower the iodine number of the stearic obtained. It is impossible to obtain a stearic of a low iodine number as well as an oleic of a high number or low cloud-point simultaneously in one step. For that purpose separation would have to be carried out in two or more steps by bringing the stearic suspension to a higher temperature and separating the precipitated oleic components in a second step. However the stearic suspension may also be heated above its melting point and allowed to recrystallize. It is, of course, also possible to separate the stearic of the first step from the water and to subject it again to the separation process. With regard to heat economics one often prefers to separate first the biggest amount of stearic at a somewhat higher temperature and then to cool the oleic in a second step.

In a one-step operation, tallow fatty acids give a stearic with an iodine number of 13–18, depending on the composition of feed and processing conditions.

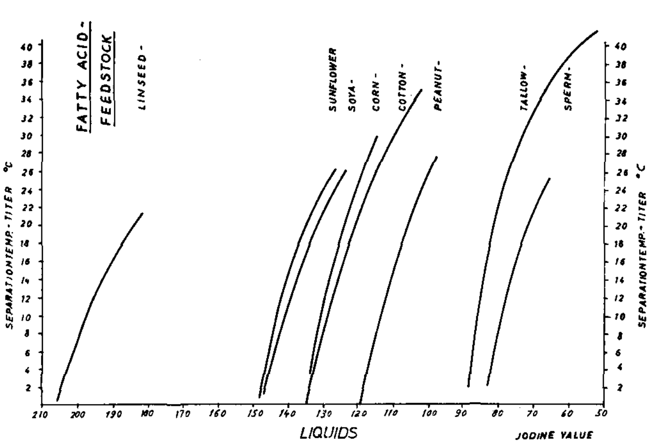

FIG. 6. Separation of several fatty acids. Relation between separation temperature and iodine value.

Operating in a second step at higher temperature one obtains stearic with an iodine number of 4–6. The titer or cloud point of the oleic corresponds approximately to the temperature of crystallization and separation.

Almost any kind of fatty material can be subjected to the process. Although the main interest may lie in the production of stearic and oleic from tallow fatty acid, it must be stressed that the process is by no means restricted to that application. For years this laboratory has been processing all kinds of fatty acid compositions in this way. Vegetable fatty acids give liquid fatty acids with higher iodine numbers.

Fig. 6 illustrates some of the processed fatty acids. It shows what iodine numbers the liquid fatty acid components have which were separated at different temperatures. The iodine values increase by 20–30 units if the separation is done at about 5C. The

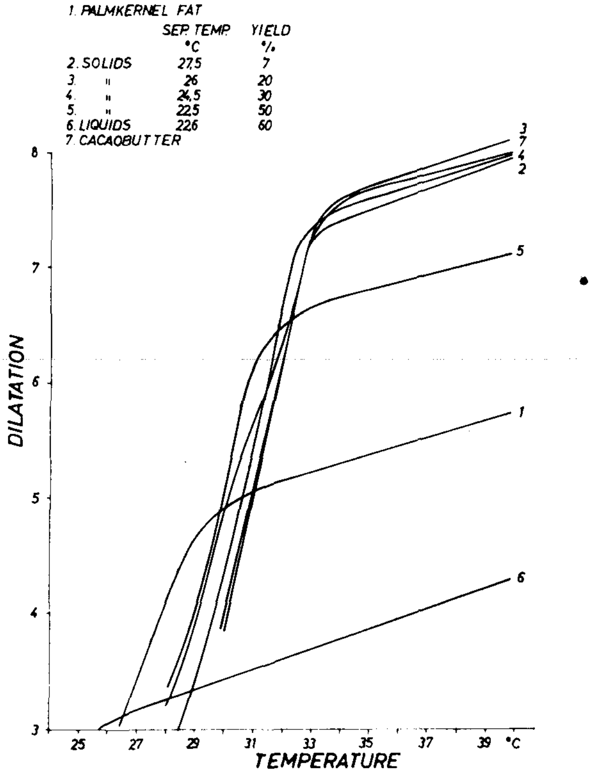

FIG. 7. Separation of palm kernel fat. Dilatation of the solids.

TABLE I

Separation of Several Fatty Acids. Composition of the Liquid Fatty Acids

Fatty Acid	IV		SV	CT[a]	Chain Length % of Liquids								
	Feed	Liqu.			C_{12}	C_{14}	C_{16}	C_{18}	C_{14}'	C_{16}'	C_{18}'	C_{18}''	C_{18}'''
Sunflower	127	146	202	3	0.2	0.3	4.8	0.6	0	0	25.6	68.2	0.3
Soya	123	145	202	4	1.0	0.7	5.1	0.6	0	0	30.8	54.1	7.7
Cotton	102	133	203	5	0.5	1.0	5.5	0.5	0	0.5	36.0	56.0	Tr
Palm	54	99	206	5	2.0	1.5	5.0	0.1	0	0	71.5	19.9	Tr
Tallow (olein)	49	90	204	4	1.0	3.0	4.5	0.5	1.5	7.0	73.5	9.0	Tr

[a] Cloud Test DIN 51 583.

titer or cloud point of the processed liquid components corresponds to the temperature of separation. Those of particular importance to industry are the liquid components of sunflower, soybean, and cotton fatty acid. Their composition and that of spermic and tallow are seen in Table I. They are liquid fatty acids of a high content of linoleic acid, which are therefore of particular interest in the manufacture of paints and varnishes. They have attained a big market and are processed on a large scale by the varnish industry and for alkyds. The solid fatty acids produced at the same time essentially consist of palmitic acid. When separating vegetable fatty acids, one generally gets products containing more than 70% of palmitic acid.

Apart from fatty acids, saturated fatty alcohols as well as fatty acid esters as sperm oil and glycerides were separated. The separation of palm kernel fat allows the production of solids with a sharp melting-point. These fractions are extremely hard, and their behavior is similar to that of cocoa butter.

Fig. 7 represents the dilatation of various fractions of that kind and shows the close resemblance with the dilatation behavior of cocoa butter. Solids of a behavior similar to cocoa butter may also be obtained from lard, tallow, or palm oil. In those cases however the process has to be carried out in several steps. Solids of those fats have the advantage of resembling cocoa butter also in their chemical composition.

The operating costs of the new process, of course, do not apply generally. Apart from the feedstock, the special conditions of the plant play a considerable role. The process needs the following utilities per ton of fatty acid, approximately: water, $30m^3$; electricity, 70 kw/hr; steam, 0.7 ton; wetting agent, about 3 kg; and salt, about 4 kg.

In Germany a processing plant for 40 tons of fatty acid a day would cost about $300,000. The process has proved to be very efficient. For years this company has been using it continuously at a rate of more than 8,000 lbs of fatty acid per hour.

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