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Hydrolysis Methods

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THE hydrolysis of fats to fatty acids and by-product glycerine is practiced extensively, as we know, by many companies but by relatively few methods. For more than 100 years fatty acids have been produced on an intentionally commercial basis. At first prolonged boiling at fat and water was utilized; later sulfuric acid became the established catalyst. In the 1890's Ernst Twitchell developed the sulfonic acid catalyst bearing his name. Additional improvements in the acid catalyst have taken place since but no major change. Meanwhile attention was given to operation at higher temperatures and pressure even in this early period. While popular in Europe, batch autoclave operations did not make much headway in this country. In the last 25 years the availability of suitable materials of co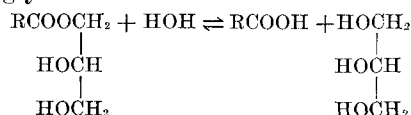nstruction, notably the stainless steels, and a background of successful continuous operations in chemicals and in petroleum aided in the successful operation of the continuous countercurrent autoclave process.

E. A. Lawrence

Hydrolysis Reaction

A brief discussion of the hydrolysis reaction itself should aid in the consideration of these methods. The general case of ester hydrolysis may be represented as:

$$RCOOR' + HOH \rightleftharpoons RCOOH + HOR'$$
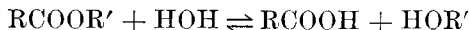
In this particular case the alcohol is glycerine with three hydroxyls. The simplest glyceryl ester would be the monoglyceride:

$$RCOOCH_2 + HOH \rightleftharpoons RCOOH + HOCH_2$$
$$|\qquad\qquad\qquad\qquad |$$
$$HOCH \qquad\qquad\qquad HOCH$$
$$|\qquad\qquad\qquad\qquad |$$
$$HOCH_2 \qquad\qquad\qquad HOCH_2$$

Since fats are triglycerides, a series of three hydrolysis steps are required to obtain free acid and glycerine. Although there are three ester linkages in the triglyceride, there is no evidence for any one being especially reactive. Neither is there evidence for a marked difference in reactivity for mono-, di-, or triesters. Both di- and mono- are found in the product from hydrolyzing mixtures (7). The same catalysts and conditions favor the reverse reaction of esterification, which also proceeds stepwise. Therefore equilibrium yields all possible reaction products and intermediates. It is interesting to note that if the fatty acids are further removed from the reaction by formation of a salt, such as the formation of soap, there would be no reverse reaction and consequently little intermediate mono- and di-ester present. Unsaponified fatty material in a soap kettle shows up as predominantly triglyceride.

a) *Effect of Immiscible Phases.* With a simple ester such as ethyl acetate, all reactants and products are mutually soluble. In the case of long chain acids such as fats, the ester and the acid are miscible as are the alcohol and water, but the fatty acids are but very slightly miscible with water and glycerine. This both helps and hinders the design of satisfactory processes and equipment. Since water and fat, the two reactants, are but slightly soluble, reaction may take place either at the interface, in the water phase due to the slight solubility of fat in water, or in the fatty phase due to the slight solubility of water in fat. Reaction takes place much more readily in solution where both water and ester are freely available to each other than it does at a water-oil interface. Therefore the reaction due to the small mutual solubility of the two phases is more important than that taking place at the interface. Since the solubility of water in fat is considerably higher than that of fat in water, the fatty phase is the most important.

Furthermore water is much more soluble in monoglycerides and in fatty acids than in the tri-glyceride ester so that its concentration in the fatty phase increases as the reaction proceeds. A triglyceride which contains no free acid exhibits an induction period as shown in Figure 1 (8). A similar phenomenon is observed during kettle saponification of refined oils. This is not a problem with most low grade raw stocks, which always contain considerable free acid.
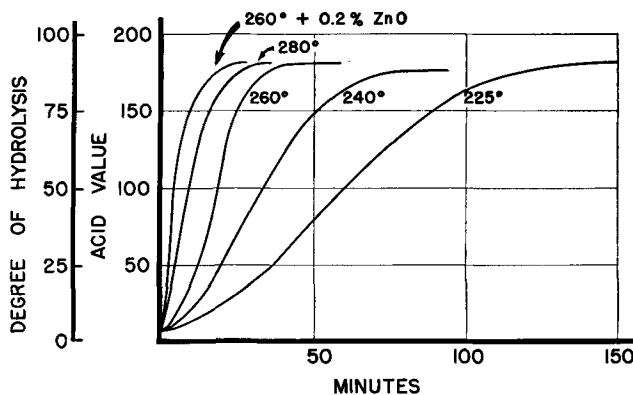
FIG. 1. Hydrolysis of beef tallow (8)

b) *Effect of Free Glycerine.* As fat is converted to fatty acid, the concentration of the reacting ester decreases and the reaction slows down. The amount of free glycerine is increasing and tends to suppress fur-

ther reaction. Since glycerine is water-soluble, the reaction can be hastened toward completion if the glycerine is removed from the oil into the bulk of the water phase as quickly as possible and replaced by more water. The hydrolysis of fats can be carried essentially to completion without using large excesses of water because the limited solubility of water and oil permits removing the glycerine from the scene of reaction. If the alcohol were oil-soluble, such as butyl alcohol, then it would remain in the oil phase and the reaction could not be forced to completion.

c) *Effect of Temperature.* Increasing the temperature not only speeds up the reaction rate but also increases the rate of diffusion of water and glycerine into and out of the fat phase. Furthermore the solubility of water in the fatty phase is markedly increased by raising the temperature as shown in Figure 2 (7).
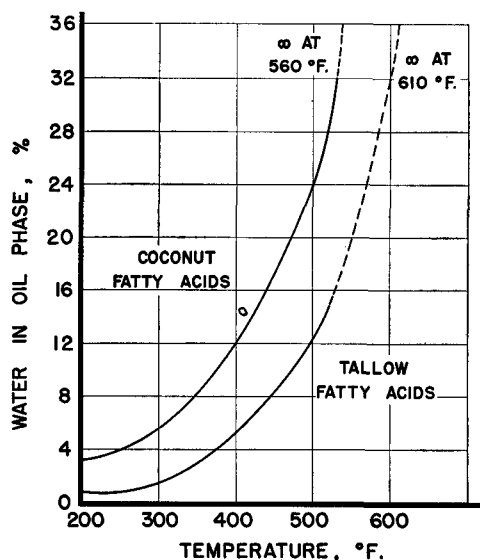

FIG. 2. Solubility of water in fatty acids (7)

Figure 1 also shows how the degree of hydrolysis may respond to the increase of temperature. The hydrolysis shows no measurable heat of reaction, and hence the equilibrium itself is not shifted as the operating temperature is changed (8).

d) *Effect of Catalysts.* In general, acid catalysts are the most effective for esterifications and for hydrolysis. Lascaray (5) attributes the superiority of the Twitchell sulfonic acid catalysts to their greater solubility in fatty oils in comparison to sulfuric or hydrochloric acids. Although basic materials are less effective (2), they are used for autoclave operations to avoid the corrosion problems attendant on the use of acid catalysts. Lascaray (5) gives the relative effectiveness of the basic catalysts as:

ZnO	MgO	CaO	LiOH	NaOH	KOH	NH$_2$OH	H$_2$O
6.0	3.1	2.3	2.0	1.7	1.4	1.1	1.0

These, of course, form metal soaps with free fatty acid and thus dissolve in the fatty phase. Figure 1 shows the effectiveness of ZnO catalyst at 260°C.

Hydrolysis Methods

Practical hydrolysis methods require consideration of both capital cost and operating expense. When a large number of different fat stocks are processed and the total volume of any one is fairly small, a batch process is indicated. When only a few different stocks

are handled and changes are at infrequent intervals, the continuous process is generally preferred.

a) *Twitchell Process.* The simplest process equipment is an open tank. In this case the boiling point of water limits the maximum temperature to 212°F. Acid catalysts of high activity are required to achieve reasonable reaction rates at this temperature. Operation at atmospheric pressure in turn permits simple tank construction from acid resistant materials such as wood, lead, and monel linings. Since the mutual solubility of the two phases is quite limited, vigorous agitation with open steam for about 15 hours is required to approach equilibrium. Usually the fat is first given a wash with sulfuric acid to coagulate and remove proteinaceous material. The splitting is carried out with a little sulfuric acid in the water as well as sulfonic acid catalyst.

b) *Multiple Stages.* In order to obtain high yields the free glycerine concentration must be kept low as shown in Figure 3 (7). However this results in a
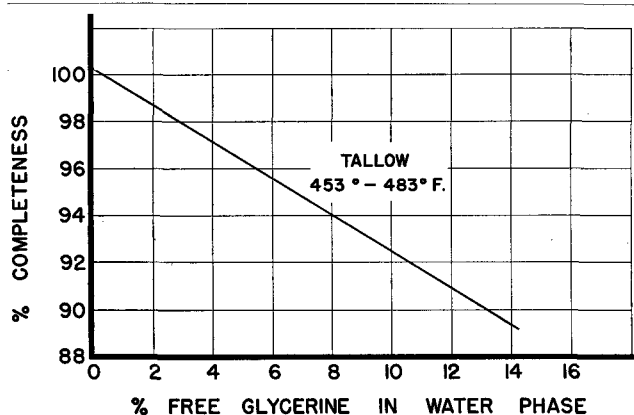
FIG. 3. Completeness of hydrolysis vs. glycerine in sweetwater (7)

sweetwater too dilute for economical recovery. By employing two stages, fresh water is used in the last stage in contact with fat already about 85% split. The resulting dilute sweetwater is then charged to another tank with fresh fat. In this manner 10-12% glycerine can be obtained economically. More stages utilized in a countercurrent manner will permit higher yields and higher concentration sweetwater. Four stages seems to be the practical maximum.

c) *Batch Autoclave Process.* By raising the temperature, the reaction rate is increased approximately 33% for each 10°C (18°F). As soon as the temperature is raised above 212°F, pressure vessels are required. Because of the corrosion problems attendant on acid catalysts, autoclave splitting is confined to the basic catalysts. Stainless steel construction and mechanical agitation are commonly used. Once it is desired to go to this more expensive construction, there is no point in stopping short of 150 p.s.i. operating pressure which corresponds to about 300°F (150°C). Temperatures up to 472°F (220°C) are common, and the required batch time is reduced to about six hours. While batch autoclave splitting is common in Europe, it has not been widely employed in this country. The preference in the U. S. is for the Twitchell method.

d) *Continuous Autoclave Process.* The move to continuous operation gets around the repeated charging and draining required by batch stagewise operation. As the temperature is increased to 500°F

Fig. 4. Continuous hydrolysis of fats to fatty acids.

(260°C), the solubility of water in fatty acid is sufficient to provide all that necessary for hydrolysis. Extraction of the released glycerine is all that is required to permit the reaction to go to completion. By using a vertical tower (3, 6) to provide countercurrent flow, the problems of high pressure packing glands for agitators can be eliminated since no such agitators are required. This in turn simplifies operation at the necessary 700-800 p.s.i. Although the catalyst increases the reaction rate as shown in Figure 1, there

is less need for a catalyst at these temperatures, and often it is omitted to simplify the processing of the resulting acids.

A flow sheet for this process is shown in Figure 4 (1). Water and fat are fed countercurrently to the tower. By exchange of heat between the two streams and by the direct injection of high pressure steam, the process is maintained at 480°-520°F. A hold-up of about 1½ to 2½ hours for the fat is common, and a resulting 96-99% split is readily obtained with up to 15% glycerine in the sweetwater.

e) *Hydrolysis with Enzymes.* The use of enzymes for the hydrolysis of fats while not commonly employed is of value for castor oil. Since the fermentation takes place at about 100°F, it yields light-colored acids without dehydroxylation or interesterification of the ricinoleic acid. It is an interesting process if not generally attractive economically.

This general review of hydrolysis methods has been directed primarily toward the principles guiding the process design. The effect of the major operating variable has been discussed as applied to both Twitchell and Autoclave methods. There was no discussion of the acidulation of refining foots as a source of fatty acids.

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Production of Fatty Acids. Separation Methods

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THE discovery and isolation of fatty acids by Chevreul in the early part of the 19th century is undoubtedly the first record of the separation of fatty acids. Since that time many methods of separating fatty acids have been developed and used in the laboratory. A few of these methods, panning and pressing, solvent crystallization and fractional distillation have achieved commercial significance and quite naturally are presented in some detail. Reference to some laboratory methods is made, especially those which may appear to have commercial potentialities. Fundamentally, separations of fatty acids may be classified as follows:

a) The separation of solid fatty acids from liquid fatty acids. For example, the separation of stearic and/or palmitic acids from oleic and linoleic acids.

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b) The separation of solid acids, as in the separation of stearic acid from palmitic acid.

c) The separation of liquid acids. As an example, oleic from linoleic acid.

Most of the methods of separating fatty acids are confined to one or two of these categories although a

few might, in certain instances, embrace all three. All methods of separating fatty acids are dependent on the variance of certain physical and chemical properties of the fatty acids or their derivatives. Probably the most important general properties of fatty acids which may be utilized to effect their separation are solidification point, melting point, vapor pressure, boiling point, solubility characteristics, and chemical reactivity. In the panning and pressing method of fatty acid separation, solidification point and solubility characteristics are the important properties whereas, in fractional distillation, vapor pressure and boiling point are of prime consideration. In solvent crystallization methods solubility characteristics are the controlling factors. It may be readily observed that the utilization of one of these general properties in a separation method will normally limit the method to one of the categories mentioned whereas a combination of these properties may permit the method to embrace all three classifications.

Panning and Pressing Method

The oldest method used in industry to separate fatty acids is the "panning and pressing" method. It is most successfully employed in the separation of fatty acids derived from animal fats to produce "commercial stearic acid" and oleic acid. Efficient operation of this method depends on utilizing fatty acids in which the solid acids are in the proper ratio to form a crystalline structure so that the liquid acids may be easily expressed. In "commercial stearic acid" this