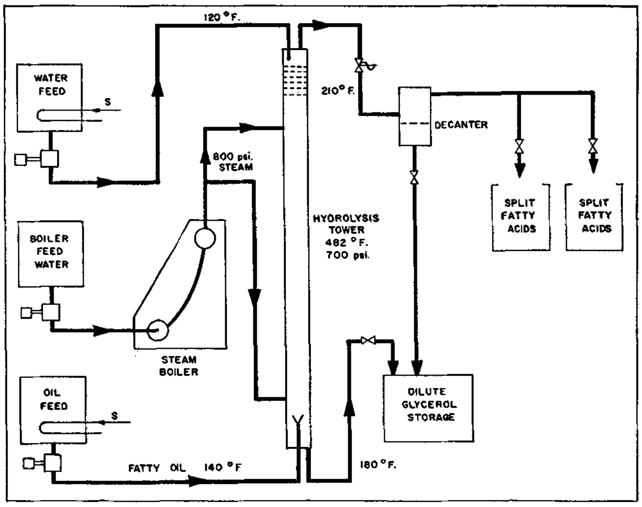

FIG. 4. Continuous hydrolysis of fats to fatty acids.

(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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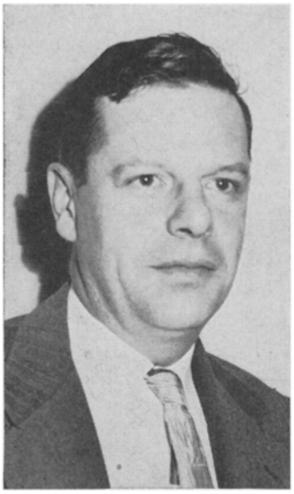
THE discovery and isolation of fatty acids by Chevreul in the early part of the 19th century is undoubtedly the first record of the separation of fatty acids. Since that time many methods of separating fatty acids have been developed and used in the laboratory. A few of these methods, panning and pressing, 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:



V. J. Muckerheide

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.

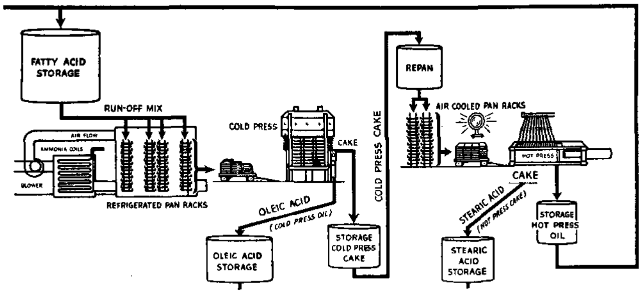
b) The separation of solid acids, as in the separation of stearic acid from palmitic acid.

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

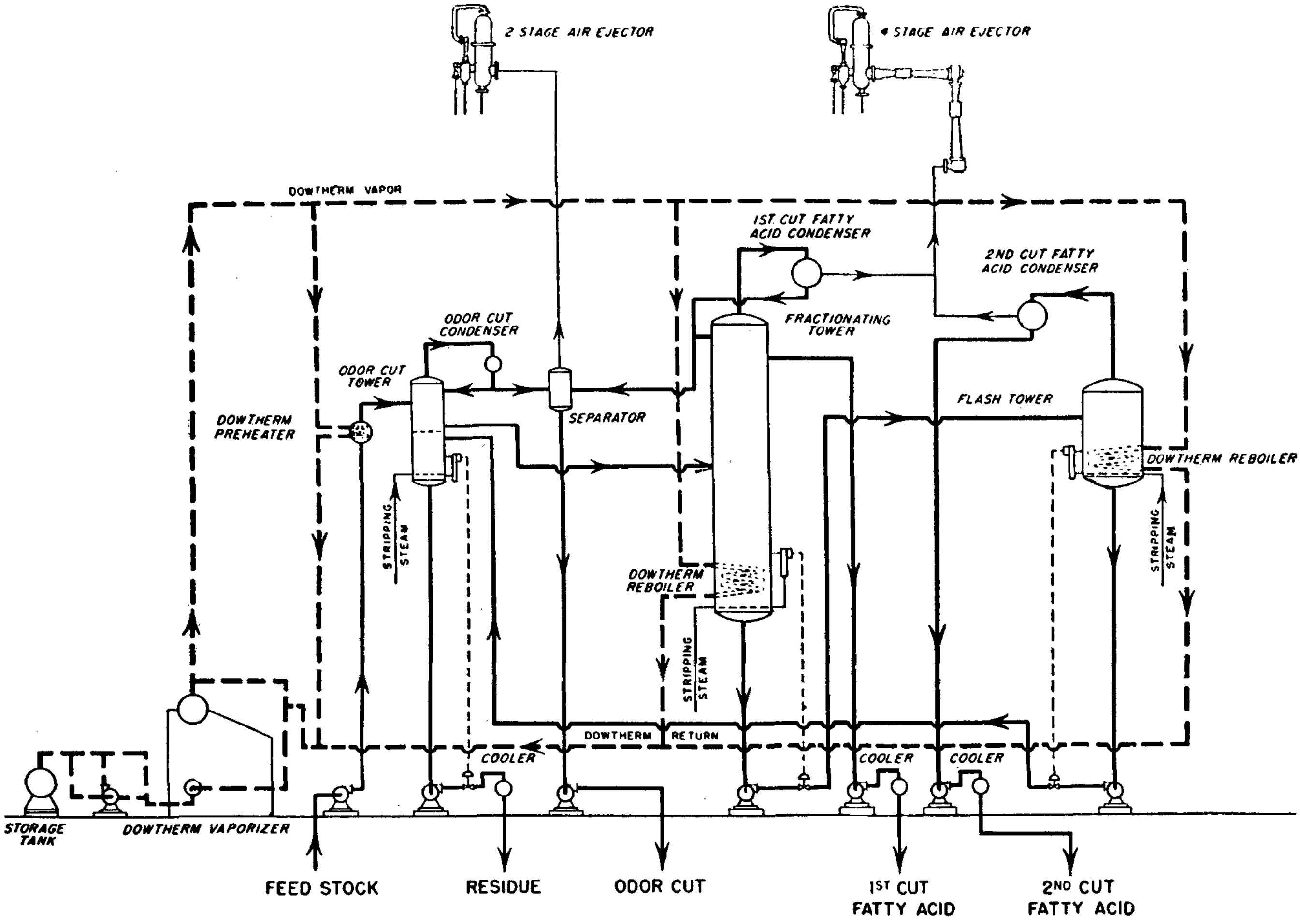


Planning and pressing method

ratio is approximately 4.5 parts of stearic acid to 5.5 parts of palmitic acid. The variation in this ratio in animal fats is sufficiently great so that care in selection or blending is necessary in order to secure a crystal structure. Fatty acid mixtures of a non-crystalline structure may be partially separated by the pressing method, but it is time-consuming and the efficiency of separation is very poor.

In operation the fatty acids are cascaded into aluminum pans, about 12 by 21 in. and 2¼ in. deep, holding about 15 lbs. each, allowed to solidify, and cooled slowly in mechanically refrigerated rooms to 36°F.-38°F. It is important that this cooling be done slowly to insure the formation of large and well-defined crystals of the solid acids. Rapid cooling results in small crystal formation and occlusion of liquid acids, thus greatly lowering the efficiency of separation. Normally this cooling period requires 6 to 8 hrs., after which the solidified cakes are removed from the pans, wrapped in burlap or heavy cotton cloths, and stacked in a vertical hydraulic ram press. Metal sheet separators placed between each two layers of cakes serve to keep the press load in place and to conduct the expressed oleic acid to the outer portion of the cake stack. The average capacity of the press is about 300 cakes. Pressure is slowly applied ranging to a maximum of 2,500 to 3,000 p.s.i., during which the greater portion of the oleic acid is removed. This cold pressing operation yields oleic acid of approximately 5°C. to 8°C. titre (dependent on the temperature of the cake during the pressing operation) and cold press cake, which contains about 20% oleic acid.

The cold press cake is melted and again allowed to solidify in aluminum pans at room temperature. These cakes are then placed in hair mat slings placed between steam-heated plates in a horizontal ram press. Pressure and a small amount of heat are applied, which remove a greater portion of the liquid acids together with some solid acids as "hot press oil," and yield "double pressed stearic acid." Similarly "double-pressed stearic acid" is converted to "triple-pressed stearic acid" with the formation of additional "hot press oil." The oleic content of "double-pressed stearic acid" is between 5% and 8% while "triple-pressed stearic acid" will range from 2% to 4% oleic acid content. The "hot press oil" is blended with the incoming fatty acids to the process. In consequence there is a constant recycling of fatty acids, amounting to about 40% of the fatty acids in process. The usual



Fractional distillation method (Armour process) acid boiling and bleaching operations are used for finishing of the solid acids obtained.

Fractional Distillation

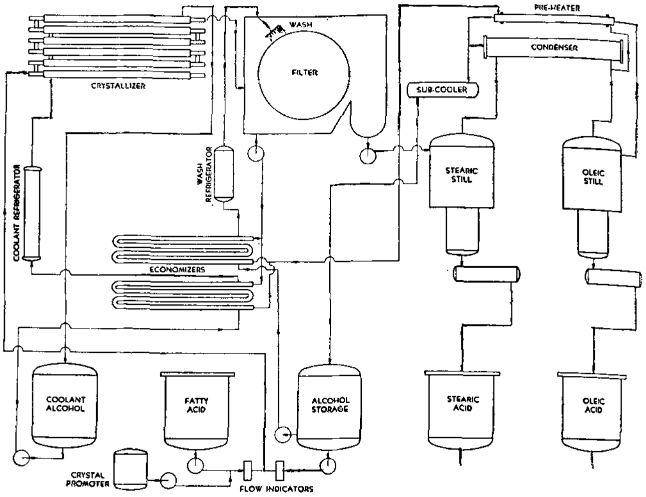
The refining of fatty acids by distillation is an old art, being used for more than a century to purify various types of fatty acids. The use of distillation methods to separate fatty acids required an investigation of the physical properties of fatty acids, especially specific heats and vapor pressures. While small scale laboratory fractional distillation of fatty acids involved only small quantities of fatty acids, relatively short heating times and glass equipment, commercial installations used large amounts of fatty acids, required special means of heating to avoid high temperatures for long periods of time, and needed corrosion-resistant materials of construction. It was probably the latter requirement that caused the most difficulty. With the rapid advance made in the field of metallurgy, newer alloys became available which would successfully resist the corrosive action of fatty acids and, in consequence, commercial fractional distillation became a reality. The ability to separate fatty acids by fractional distillation is limited by the differences among the vapor pressures of the fatty acids. Fractional distillation is most effective when used to separate fatty acids of four to six carbon atoms difference in chain length. Separation of saturated from unsaturated acids of equal carbon atom chain length is not possible. The efficiency of separation is controlled by the number of plates or bubble cap trays in the column and the reflux ratio. Theoretically it is possible to effect a complete separation of fatty acids having different boiling points. However a compromise in efficiency of separation must be made because economic considerations, practical height of column, and number of trays; and a reasonable reflux ratio must be taken into consideration in a commercial installation.

Typical of a continuous commercial fatty acid fractionating distillation process is the one introduced in this country by Armour and Company (1) with actual plant design by Foster Wheeler Corporation (2). In general, this process involves initial stripping of the fatty acids followed by fractionation in a column fitted with a plurality of bubble cap trays in which the fatty acids are separated by virtue of their difference in boiling points. The residue is, or very high boiling fatty acids from this column are fed to a final stripping tower where they are removed, leaving a final residue.

In operation, fatty acids are fed to a pre-heater, heated by Dowtherm vapor, raised to about 400°F., and discharged to the first column, where, under a reduced pressure of 35 mm. Hg. and live steam injection, most of the very low boiling odorous fatty acids and low boiling unsaponifiable fractions are removed. Bubble cap trays fitted in this first column permit a degree of rectification. The fatty acids, stripped of low boiling fractions, are fed into the main fractionating column. A four-stage air injector with barometric inter-condensers maintains about 5 mm. Hg. pressure at the top of this column. A Dowtherm-heated reboiler in the base of the column provides the necessary heat for vaporization of the fatty acids. The overhead distillate from this column, comprising the low boiling fatty acids and odor bodies, is condensed and combined with the distillate from the first column. Reflux is returned to the top of the column, and a liquid side-stream of fractionated fatty acids, constituting the first fatty acid cut, is taken off near the top of the column. Purity of this first fatty acid cut is dependent on the design of the fractionating column, and to some extent on the reflux ratio and rate of feed. Normally a purity of 85% to 90% is obtained.

The bottoms from the main column are pumped to a flash tower where the second cut of fatty acids is removed by simple vacuum-distillation. The residue from the flash tower is pumped to the initial column for a final stripping action. A bubble cap tray located in the middle of this column prevents mixing of the residue with the initial feed stock. Automatic controls and instrumentation are used throughout the process. Capacities range from 3,000 to 4,000 lbs. per hour of feed stock. Cottonseed fatty acids, either as such or hydrogenated, palm oil fatty acids, and coconut oil fatty acids constitute ideal feed stocks for this process.

Solvent Crystallization



Solvent crystallization method (Emersol process)

The inherent limitations of the panning and pressing method and of the fractional distillation process prompted the investigation of other methods of separation of fatty acids. Solubility characteristics of fatty acids in various solvents indicated possibilities in the field of solvent separation. Solvent methods involving selective action, in which the fatty acids remain in a liquid state, give rather poor separation efficiency because of the mutual solubility characteristics of the fatty acids. A study of the solubilities of individual acids in various solvents was of little value because of the intersolubilizing effects which occurred in mixtures. While it is well known that a countercurrent system of solvent extraction may be employed to obtain a fairly efficient separation of fatty acids by use of a large number of passes, the practical application is not economically feasible. The solvent crystallization method of separating fatty acids in which one component acid of a fatty acid mixture is crystallized overcomes to a large extent the effects of mutual solubility. Solvent crystallization methods may be applied to almost any fatty acid mixture, provided one of the component acids is capable of being removed in the solid state from a solution of the remaining fatty acids. Thus saturated acids may be separated by virtue of differences in solubility due to differences in carbon atom chain length, or acids of same carbon atom chain length may be separated on account of differences in solubility, caused by differences in degree of unsaturation. Probably the greatest efficiency of a solvent crystallization process is realized in the separation of saturated fatty acids from unsaturated fatty acids.

The first continuous commercial fatty acid solvent separation process was the "Emersol Process" (3) and is typical of solvent crystallization methods. Introduced and designed by Emery Industries Inc. (4), this process involves the controlled crystallization of fatty acids from a polar solvent. The crystallized acids are continuously removed by filtration, yielding a filter cake and filtrate from which the solvent is removed to obtain the separated acids.

In a typical operation involving the separation of "commercial stearic acid" from oleic acid, fatty acids derived from animal fats are continuously mixed with 90% methanol and pumped to a multi-tubular crystallizer. A crystal promoter may be added during this mixing operation. The crystallizer consists of a bank of jacketed stainless steel tubes fitted with slowly rotating scraper blades. Cooling of these tubes is accomplished by circulating refrigerated methanol through the jackets. The fatty acid-methanol solution enters the crystallizer at about 80°F., flowing countercurrent to the incoming refrigerated methanol, and is cooled to about 14°F. During this cooling the solid acids crystallize from the solution, the scraper blades promote the proper rate of heat transfer to insure the formation of filterable fatty acid crystals. Leaving the crystallizer, the slurry or crystallized mass flows to an enclosed rotary vacuum filter, where the solid acids are removed and washed with fresh methanol, while the liquid acids remain in the filtrate. The solid filter cake containing about 65% solvent is discharged to a steam-jacketed trough, where it is melted and then pumped to the solvent removal still. The filtrate is passed through a heat exchanger in countercurrent flow to methanol, where approximately 65% of the total refrigeration is recovered. The filtrate then flows through a pre-heater and thence to the solvent recovery stills. The design of the solvent recovery stills (5) is unique in that the bulk of the solvent is recovered from the fatty acids in a calandria at a relatively low temperature and at atmospheric pressure. The remaining solution of fatty acids passes down a column fitted with bubble cap trays, where fractionation of the methanol is accomplished by steam rising from the reboiler at the base of the column. In this manner the concentration of methanol is reduced as the temperature rises, and as a result a mixture of fatty acid and very dilute methanol enters the reboiler. A settling zone is provided in the reboiler; the fatty acids are removed continuously, and the water is reboiled to provide stripping steam.

Refrigeration is supplied by a two-stage ammonia compressor driven by a steam turbine, which is equipped with a variable speed-control device. This permits a variation in refrigeration, which effects a control over the temperature to which the solution of fatty acids and solvent is cooled. Exhaust steam from the turbine is used to heat the calandrias of the solvent recovery stills.

In normal operation commercial stearic of 5.0 to 6.0 iodine value and oleic acid of 2°C. to 5°C. titre are obtained. The process is equipped with full and completely automatic controls and instrumentation. Construction throughout is of stainless steel. Capacities range from 2,000 lbs. per hour to 5,000 lbs. per hour. Separation of fatty acids from many types of fats and oils may be accomplished by variation in processing conditions.

Other Methods

In a general discussion of production processes of separating fatty acids, reference should be made to certain methods which at present are not of commercial significance but may have future potentialities. Excluding well-known classical laboratory methods of fatty acid separation, such as the Twitchell lead soap method, two recently developed methods, urea complex formation (6, 7) and liquid thermal diffusion (8) may be mentioned. Methods of separating fatty acids involving chemical modification or compound formation—for example, the separation of the methyl (9) esters of fatty acids, the fractional precipitation of solid glycerides formed by directed interesterification of mixed glycerides (10), and the separation of fatty acids by preferential neutralization (11)—may also be mentioned in passing.

Separation of a mixture of fatty acids by the urea complex method involves the intimate contacting of a solvent solution of the fatty acids with a saturated aqueous solution of urea under conditions which cause an adduct formation of one of the fatty acids, which precipitates and is removed by filtration. The adduct is decomposed by addition of water and heating, and the fatty acid is recovered. The urea adducts formed have varying degrees of stability, which is dependent on the carbon atom chain length and the configuration of the molecule. It is postulated that the urea molecules form interpenetrating spirals about the fatty acid molecule and the amount of hydrogen bonding and the degree of van der Waals' forces between the urea and the fatty acid molecule account for the degree of stability. Separation of saturated fatty acids from unsaturated fatty acids as well as separation of unsaturated fatty acids having different degrees of unsaturation by the urea complex method have been reported (12). Urea adduct formation of fatty acids is normally carried out at room temperature, which may be considered an advantage; however the low concentration of fatty acids in the solvent (8% to 10%) and the large amount of urea required (a weight ratio of about 3 to 1) constitute a disadvantage since considerable bulky material must be processed and reclaimed per pound of fatty acids separated. Efficiencies of separation are reported to be about equal to those obtained by solvent crystallization methods.

The application of liquid thermal diffusion to fatty acids, specifically tall oil (8), has indicated promise as a means of separating fatty acids. The apparatus used in the liquid thermal diffusion method consists essentially of two concentric tubes of suitable length having a one millimeter annular space. This space is filled with fatty acids, the outer tube is heated either by a steam or electrical jacket, and the inner tube is cooled with water. These conditions result in a temperature gradient across the liquid ranging from 40°C. to 80°C. This temperature gradient induces the diffusion of certain molecules from the hot wall to the cold wall of the tubes. Convective flow due to density differences produced by the temperature differential causes the diffused molecules to flow upward or downward and thus effect a separation. The theoretical principles of liquid thermal diffusion have not been fully developed. Factors which affect the degree of separation in the thermal diffusion process are uniformity of size of the annular space, temperature differential, and time required for diffusion. It appears that this method may be adapted for continuous operation.

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Ester Reactions of Fatty Materials[1]

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REACTIONS involving ester linkages of fats and oils are among the most important in the chemistry of fatty acid derivatives. Hydrolysis of esters under alkaline conditions, the familiar saponification of fats and oils, has been practiced for centuries. This paper will cover the nonhydrolytic ester reactions: esterification, alcoholysis, acidolysis, and interesterification. These reactions are of far more recent origin and have been recognized for approximately one century. However it has only been within the past few decades that they have assumed technical importance. Alkyd resins, rubber-like polyesters, improved lard for shortening, and nonionic surface active agents, to improve shortening efficiency and soften bread, represent only a few of the products dependent upon these ester reactions.

M. W. Formo

General Scope and Chemistry of the Ester Reactions

There are four closely allied reversible reactions involving addition or interchange of alkyl radicals on the carboxyl residue of fatty acids. These reactions, which have much in common, are as follows:

1. Esterification is the condensation of an acid and an alcohol to give an ester and water; the reverse reaction is hydrolysis.

$$RCOOH + R'OH \rightleftharpoons RCOOR' + HOH$$

2. Alcoholysis involves the replacement of the alkyl group of an ester by another through interaction of the ester and an alcohol. The reaction is frequently described in terms of the added alcohol, e.g. methanolysis, glycerolysis, etc.

$$RCOOR' + R''OH \rightleftharpoons RCOOR'' + R'OH$$

3. Acidolysis, in an analogous way, is the substitution or exchange of acyl groups of esters through the reaction of an ester and an acid.

$$RCOOR' + R''COOH \rightleftharpoons R''COOR' + RCOOH$$

4. Interesterification, sometimes termed ester interchange or trans-esterification, is the exchange of acyl and alkyl groups between a pair of esters.

$$RCOOR' + R''COOR''' \rightleftharpoons RCOOR''' + R''COOR'$$

There has been some confusion in the literature regarding the nomenclature of these related reactions. Some authors use the terminology, "trans-esterification reactions," broadly to describe alcoholysis, acidolysis, and interesterification. Others use the term "interesterification reactions" in a similar broad sense (German "Umesterung"). It is becoming more common practice to use the term "trans-esterification" as a synonym for interesterification or ester-interchange to describe the exchange of acyl and alkyl groups between a pair of esters. Such terminology will be adhered to in this discussion.

The close relationship between esterification, alcoholysis, and interesterification is illustrated by comparison of the equilibrium constants for homogeneous reaction. Normally we do not have sufficient data to calculate all equilibrium constants, but theoretically the point of equilibrium in both alcoholysis and interesterification reactions can be calculated from the simple esterification constants.

Study of esterification and hydrolysis provided some of the earliest classical examples of reversible equilibria. At equilibrium in a homogeneous reaction the relationship between concentrations of reactants and products is represented by the familiar esterification constant.

$$\text{Acid} + \text{Alcohol} \rightleftharpoons \text{Ester} + \text{Water}$$

$$\frac{[\text{Ester}] \times [\text{Water}]}{[\text{Acid}] \times [\text{Alcohol}]} = \text{K esterification}$$

Table I illustrates the relationship of the esterification equilibrium constant to the alcoholysis and interesterification equilibria. Knowledge of esterification constants would permit calculation of the equilibria in both alcoholysis and interesterification reactions.

Several reviews are available covering the ester reactions (1, 2, 3, 4, 5).

Esterification Reactions

There are four primary methods for direct preparation of esters:

1. reaction of an alcohol and an acid with elimination of water;

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[1] Technical Paper No. 130 from the Archer-Daniels-Midland Company.