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Esterification and Interesterification

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ABSTRACT

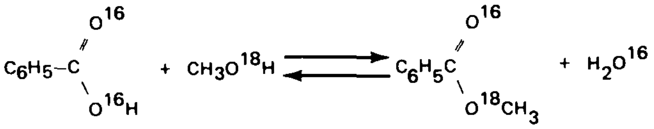
A versatile and large group of fatty acid esters are prepared from monohydroxy alcohols (C_1 to C_{22} members), glycols (ethylene and propylene glycols and others), etherglycols (many polyoxyethylene glycols), triols (glycerol and others), tetraols (pentaerythritol and others), polyglycerols, carbohydrate materials (sorbitol, sorbitan, sucrose and others). The two most important direct esterifications of fatty acids are those done with monohydroxy alcohols (methanol, butanol, etc.) and glycerol itself. Esterifications of these materials are carried out with or without the use of catalysts. For edible ester products, the choice of catalyst is determined by (a) rate of reaction promotion permitted by the use of the catalyst; (b) color of product obtained; (c) ease of removal of catalyst; (d) toxicity of catalyst, and perhaps; (e) other factors including promotion of acrolein formation from glycerol, loss by volatilization at high temperatures, inactivation above certain threshold temperatures, and catalyst corrosivity on the materials of construction of the esterifier. In certain instances the last factor may indeed be the paramount one in a particular catalyst choice for a direct esterification. Industrial production of methyl esters is principally by a process of interesterification called methanolysis. Polyols require conditions for complete esterification that are vigorous and severe. The two most important interesterification methods used in the fatty acid industry are the methanolysis of fats and oils for the production of methyl esters and the glycerolysis of fats and oils for the production of three kinds of so-called "monoglycerides," namely the 40%, 60% and 90% monoglycerides.

Since the original direct esterification in 1844 by Pelouze and Gelis of glycerol with butyric acid (1), both esterification and interesterification have been developed to the state where today they collectively constitute the most widely used methods for the production of fatty acid derivatives. Applications appear to be about equally divided among edible and nonedible industrial products.

The versatile and large group of fatty acid esters are prepared from monohydroxy alcohols (C_1 to C_{22} members), glycols (ethylene and propylene glycols and others), etherglycols (many polyoxyethylene glycols), triols (glycerol and others), tetraols (pentaerythritol and others), polyglycerols, carbohydrate materials (sorbitol, sorbitan, sucrose and others).

Esterification, according to all the textbooks, is the reverse reaction of hydrolysis, and in the case of glycerol it is the reverse reaction of fat splitting. For many years it was recognized that in the reaction the mechanistic course could correspond to one or both of two separate routes.

In short, does the water that is produced arise from the hydroxyl group of the acid or from the hydroxyl group of the alcohol? An examination of the course of the esterification of benzoic acid and methanol with radioactive oxygen atoms (2) proved out this point: the water is formed from the hydroxyl of the acid and the hydrogen of the alcohol:



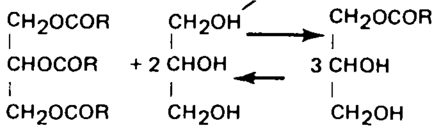
$$C_6H_5{-}C(=O^{16})O^{16}H + CH_3O^{18}H \rightleftharpoons C_6H_5C(=O^{16})O^{18}CH_3 + H_2O^{16}$$

Perhaps the most important direct esterifications of fatty acids are those carried out with monohydroxy alcohols (methanol, butanol, etc.) and glycerol itself. By no means does this exhaust the list of important directly esterified products. Esterifications of these alcohols are carried out with or without the use of catalysts. For edible ester products, the choice of catalyst is determined by: (a) rate of reaction promotion permitted by the use of the catalyst; (b) color of product obtained and need, if any, to bleach or decolorize; (c) ease of removal of catalyst; (d) toxicity of catalyst; (e) promotion of acrolein formation (from acidic catalysts with glycerol); (f) loss of catalyst by volatilization above certain temperatures; (g) catalyst inactivation above certain threshold temperatures or in the presence of certain impurities; and (h) catalyst corrosivity on the materials of construction of the esterifier. In certain instances the last factor may indeed be paramount in a particular catalyst choice for a direct esterification.

Industrial production of methyl esters is principally by a process of interesterification called methanolysis. When fatty acids are converted to methyl esters directly, the acids are usually cheap source materials such as low grade fatty acids or acidulated soapstocks obtained in the refining of vegetable or animal fats and oils like soybean, coconut, cottonseed or tallow (3). Direct esterifications of low grade or other fatty acids to methyl esters usually involve acid-catalyzed batch operations in which from ca. 3–10 molar quantities of CH_3OH/fatty acid are used with fractionation of the evolved vapors, return of separated condensed methanol, and elimination of the water. Soapstocks, since they contain 15–25% mono-, di-, or triglycerides, are best converted to methyl esters by two-step processes. One method consists of first Twitchell batch splitting the acidulated soapstocks, removing the glycerol, and directly esterifying the resulting acids with Twitchell type catalysts, whereby ca. 94% conversion to methyl esters can be readily achieved. Otherwise, the acid-catalyzed methyl esterification of unsplit acidulated soapstocks affords only 70–76% yield. Another method (4), perhaps better in some respects, is first to esterify the free fatty acids in the acidulated soapstocks uncatalyzed with the proper amount of added glycerol in the range 210–230 C at 5–10 mm pressure, followed by interesterification of the triglycerides so produced with methanol using NaOH, KOH or ZnO.

Polyols require conditions for complete esterification that are both vigorous and severe. The uncatalyzed triesterification of glycerol is somewhat time-consuming; finishing off temperatures are ca. 250 C compared to catalyzed esterifications which are finished off at ca. 200 C. For pentaerythritol (a tetraol), finishing off temperatures are between 270–300 C, depending upon the catalyst used and the application intended. Vacuum and perhaps a sparged inert gas are used for water removal.

The two most important interesterification methods used in the fatty acid industry are the methanolysis of fats and oils for the production of methyl esters, and the glycerolysis of fats and oils for the production of three kinds of so-called monoglycerides, namely, the 40%, 60% and 90% "monoglycerides." Glycerolysis is usually done without a solvent for edible products; it is catalyzed with alkaline catalyst like sodium hydroxide, sodium ethoxide, occasionally lime (for better color of product). The reaction is reversible and the textbooks indicate it to be a simple, straight-forward reaction, but in practice it is tricky and difficult to manage:



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 2\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \rightleftharpoons 3\begin{array}{l} CH_2OCOR \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Current thinking about glycerolysis of fats is that the fatty acid acyl groups distribute themselves statistically among all the available hydroxyl groups in fat-glycerol mixtures with no regard to preference for primary or secondary hydroxyls, and that the optimum solubility of glycerol in any fat at prescribed temperatures limits the maximum conversion to monoglyceride that can be obtained by such interesterifications (5). While neither assumption is exactly true, the assumptions hold up reasonably well for some practical applications. It is now known that the preference for the primary and secondary hydroxyls of glycerol is not equal in either direct or interchange esterification (6). Furthermore, the assumption that the formation of maximum monoglyceride that can be obtained is determined by the solubility of glycerol in triglyceride fat is subject to misinterpretation. During glycerolysis the composition of the reaction mixture changes as reaction progresses; i.e., 1-monoglyceride content increases as triglyceride content diminishes, and the solubility of glycerol in the near equilibrium mixture is, presumably, much higher than it is in the triglyceride starting material.

Thus, conclusions based upon the solubility of glycerol in the starting materials are not sufficiently valid when used to predict the optimum ratios of miscible reactants for conversion to monoglycerides. Actually, the determination of solubility of glycerol in fats without interchange catalysts present is not possible at temperatures above about 200 C since uncatalyzed interchange has already commenced at these temperatures. If, indeed, the assumptions were true, it should be possible from existing data and statistical calculations to expect the reaction of hydrogenated cottonseed oil and glycerol at 250 C with 40% glycerol based upon the weight of fat used, to afford a 70% monoglyceride/30% diglyceride product. This is never achieved in the commercial nonsolvent method of production. (Usually 58–62% is the optimum yield under these conditions.) Failure to achieve the predicted yields is due to the inapplicability of several of the basic assumptions on which these data were calculated, but, also, to the reversion of monoglyceride which occurs at the point of reaction completion before catalyst neutralization or after if neutralization is incomplete. During the cooling which precedes glycerol removal (by either washing or vacuum distillation), glycerol is less soluble in the fatty phase and separates into the lower layer. This shifts the equilibrium somewhat and diglyceride and triglyceride are regenerated. Even catalyst neutralization does not guarantee that reversion will not be encountered. Thus, the catalyst neutralization and removal of glycerol is the critical part of the reaction and must be carried out with care and precise control.

Although yields of monoglycerides by usual nonsolvent methods of production are limited to under 70% total monoglycerides, the use of solvents for the glycerolysis reaction enables a much higher conversion. Illustrative of the advantage of employing solvents is work carried out on sunflower oil (7). Heating at 115–120 C for 3 hr using 10 parts of oil and 20 parts of glycerol with 0.3 parts $NaHCO_3$ catalyst in excess pyridine afforded, after removal of the excess glycerol upon reaction completion, a 75% α-mono- or 83% total monoglyceride yield; the same ratio of reactants without a solvent yielded 52% α-mono- and 58% total monoglycerides.

The advantage of pressure in carrying out glycerolysis is noteworthy. The effects appear to aid in the attainment of homogeneity and thus, yields are improved. Castor oil glycerolysis is claimed (8) to give 82% α-monoglyceride content after 2 hr at 240 C with 800 g of the oil and 2000 g glycerol, if carbon dioxide, probably a coblanketing catalytic agent, is used at 100 PSIG. Under similar conditions coconut oil is said to give 74.5% and peanut oil 73% α-monoglycerides.

The highest commercial grades of monoglycerides produced by glycerolysis are the so-called 60% monoglycerides; 90% monoglycerides are produced by using molecular distillation, an efficient separative method for this purpose.

The production of fatty acid esters is generally done in versatile batch equipment that is used industrially for a variety of products with several catalysts. Acid resistant materials of construction such as Monel or some of the newer metals are required for the esterifiers used for high temperature direct esterifications; stainless steel of the 316 type is entirely satisfactory for alcoholysis reactions (although 304 type stainless steel or even ordinary carbon steel have been used for equipment used only for methanolysis). A compromise choice for a versatile unit would be one constructed from Monel or perhaps several of the newer highly corrosion resistant alloys "E-Brite," Incoloy 825 or Carpenter 20Cb (see E.E. Rice's paper). In some cases, highly acidic catalysts like sulfonic acids, sulfuric acid can be replaced by less severe ones such as hypophosphorous acid, dibutyl tin oxide and others.

Internal coils heat the contents of the esterifier with 150 PSIG (185 C) or 200 PSIG (200 C) steam; the coils are also used for circulating cooling water. For ultimate reaction temperatures at 280–300 C, such as during the finishing off stages of polyol esterifications, the unit is equipped with a Dowtherm heating jacket. It is also designed to be used at pressures up to 100 PSIG (for certain low pressure ion-exchange resin-catalyzed esterifications without removal of water), and to withstand vacuum operation down to 0.1 mm Hg in order that removal of water of esterification be facilitated, and the excesses of low boiling hydroxylic or carboxylic components be readily removed by vacuum distillation. Basket type mesh enclosures to hold heterogeneous esterification catalysts assure further use versatility. Provision to monitor layer separation directly from the esterifier or separating tanks including illuminated sight gages below them is required.

In practice, esterification of alcohols, glycols or glycerol is generally accomplished with a mild acid or metallic catalyst in the hydroxylic component part of the charge and included in the charge of the excess acid in the case of glycerol triesterifications. Esterification procedures vary considerably according to the product desired and its quality. Use of temperature, azeotropic esterification, or of vacuum (if boiling point of alcohol or glycol permit it) are employed to remove the water of esterification and permit the reaction to proceed to completion. In the esterification of low boiling glycols, such as ethylene and propylene glycols, it is customary to separate the evolved vapors through a packed fractionating column, to discard the water, and to return any separated glycol to the esterification unit. With glycerol or with polyols like pentaerythritol, finishing off temperatures as high as 260–300 C may be required. The excesses of hydroxylic or carboxylic components remaining after esterification is complete are usually distilled off under reduced pressure after neutralization of the catalysts (acids with lime, alkalies with phosphoric acid). Some operators use inert stripping gases such as nitrogen to facilitate removal of low boiling components.

For process control in the batch esterification of fatty acids with the use of excess alcohols in the charge, the determination of acid value (AOCS Te-1a-64) is generally employed; for the esterification of glycerol or polyols where excess fatty acid is used in the charge, the determination of hydroxyl value (AOCS Cd-13-60) is appropriate. Obviously, neutralization of either acidic or alkaline catalysts is required after esterification is complete if the ester is to be distilled; occasionally inert or innocuous catalysts are left in the ester, but most frequently it is desirable to remove them by neutralization and/or clay bleaching (which also improves the color of the crude ester), because most catalysts are capable of reverting esters. Tin, antimony, lead and arsenic-containing catalysts are removed because of their toxicity. Catalyst removal may be monitored by the analysis of certain trace metals by atomic absorption analytical methods, applicable to Sn, Hg, Ti, Pb, Cd, B, P, Ca, Mg, K, Na and several others. Final product quality for fatty acid esters is generally described by means of saponification value (AOCS T1-1a-64), acid value, hydroxyl value, and fatty acid distribution, although the latter is rarely a purchase specification. Trace metal content, color (Gardner: AOCS Td-1a-64; APHA: AOCS Td-1b-64) and color stability (AOCS Td-3a-64), peroxide value (AOCS Cd-8-53), particularly for edible esters, and ash content (AOCS Tm-1a) are other common specification criteria for fatty acid esters.

Sucrosolysis

The direct esterification of sucrose is limited by the tendency of sugar to carmelize if subjected to temperatures above 105 C. Although some sugar esters have been produced by the sucrosolysis of mono- and diglycerides (9), when these products are produced industrially on a small scale they are generally made from methyl esters. Sucrosolysis of methyl esters appears to be the most satisfactory method for the preparation of sugar esters, and much of the technical literature deals with innovations with and without solvents and with reaction conditions for efficient conversions. During the late 1950s and in the 1960s, attempts were made to conduct methyl ester interchanges in solvents such as dimethylsulfoxide (10,11), dimethylformamide (10,12–17), substituted morpholine or piperidines (18), or dimethylbenzylamine (19). A British patent (20) in 1963 described the use of phenyl esters and involved the elimination of phenol by fractional distillation from a nonsolvent suspension of phenyl esters and potassium carbonate at 110–120 C/0.1–0.3 mm. In an effort to avoid the use of expensive and troublesome solvents and to permit the use of somewhat higher reaction temperatures than ordinarily employed, Osipow and Rosenblatt (21) suggested the utilization of a "micro-emulsion" process for the preparation of sucrose esters. Sucrose, methyl stearate, sodium stearate and potassium carbonate suspended in propylene glycol were microdispersed until a transparent emulsion was formed. Using a starting molar ratio of 1.5:1:0.9 for sucrose, methyl stearate and sodium stearate, the slow distillation of propylene glycol was continued until reaction completion. The product assayed 85% sucrose monostearate and 15% sucrose distearate. Feuge and coworkers (9) interesterified melted sucrose with esters like methyl "Carbitol" palmitate, monopalmitin, distearin and 40% technical "monoglycerides" at temperatures of 170–187 C without exorbitant decomposition using lithium oleate or mixtures of sodium, potassium or lithium soaps as emulsifier-catalysts. With lithium oleate the products were 90% of tetraesters or higher; lower esters could be produced by blending the emulsifier system to include sodium and potassium oleate soaps. A German patent assigned to Tate and Lyle, Ltd. (22) describes preparation of sucrose monoesters from a nonsolvent media at 125 C. The process involves sucrosolysis of methyl esters such as those obtained from tallow with K_2CO_3 highly emulsified through the use of an emulsifer system consisting of sucrose monoester and tallow fatty acids. More recently, a nonsolvent, two-step process has been developed (23) for the preparation of sucrose polyesters (SPE) which permits use of less soap emulsifiers than heretofore based upon the use of metallic sodium or potassium or their hydrides added to the mixture of sucrose, methyl esters and soap at temperatures as low as 130 C. In the first step methyl esters and sucrose at a 3:1 molar ratio are reacted with potassium soap emulsifier to form low sucrose esters. In the second step, more methyl esters are added and reacted to produce SPE in yields up to 95% based on sucrose.

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Materials of Construction in the Fatty Acid Industry

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ABSTRACT

The basic material of construction for the tankage and reactors that are used in the fatty chemical industry is one or another variant of the 300 series stainless steels. The use of these alloys essentially eliminates the possibility of iron and other metal contaminations which may either degrade the product or catalyze undesirable oxidation and other side reactions. With certain exceptions, it has been found that Type 304 stainless steel may be used in fatty chemical processing at temperatures up to 150 C and Type 316 stainless steel for tanks and vessels designed for use above that temperature. Where welding is involved in the fabrication of equipment designed for high temperature usage, it has been found necessary to use either a special low carbon stainless steel or an alloy which contains an extra ingredient that will inhibit carbide precipitation in the weld area since such precipitation usually results in a point of corrosion and ultimate failure. In the fabrication of pressure vessels, it is normal practice to use carbon steel plates of suitable thickness that have a minimal amount of the desired alloy bonded to the surface rather than fabricate of solid alloy. This not only reduces the cost of the vessel but adds greatly to the strength of the sheet since most high alloys lose tensile strength rapidly as temperatures are increased while carbon steel retains strength until very high temperatures are reached. In addition to the 300 series stainless steels, certain highly specialized alloys such as Inconel 825, Carpenter 20 Cb, or Monel are frequently used for extreme acid conditions. The lower cost of aluminum as compared to a high alloy makes it attractive for storage tanks but it can be used only when materials contain no moisture, since even traces of water accelerate the rate of corrosion and rapidly render the tank unusable. New materials on the scene are fiberglass-polyester tankage and applied linings of the phenolic or the epon-epoxy type. These materials do not have a wide application, but where their use is possible, it is a lower cost answer to the problem of iron contamination.

If it could be said that there are basic metals for the fatty chemical industry, they would have to be two of the so-called 18-8 series austenitic stainless steels, Type 304 and Type 316 in one or another of their variant forms (Table I).

Typically in this industry, Type 304 stainless steel is used for fatty chemical processes where the temperature does not exceed 150 C, and Type 316 is used for temperatures above this level. The principal difference in these two alloys is that Type 316 has added 2 to 3% molybdenum, which greatly improves resistance to corrosion particularly at elevated temperatures. Since this alloying component will act in much the same way as excess chromium in the promotion of a ferritic structure, the nickel is usually increased slightly in order to keep the alloy in the austenitic form, and consequently it remains less subject to intergranular corrosion as well as retains the nonmagnetic property that is typical of austenites.

One problem of any alloy containing both chromium and carbon is the precipitation of a chromium carbide as the alloy is subjected to what is called the sensitizing temperature range of 566 to 871 C, a temperature range that will always occur during any type of welding. In this range, the carbon leaves solution in the austenite and selectively reacts with chromium for precipitation as the carbide along grain boundaries. This leaves the area immediately adjacent to the carbide grain deficient in chromium since the carbon will tie up 17 times its own weight of this metal. This renders the boundary less resistant to corrosion, and the end result is eventual weld area failure. In extreme cases involving severe corrosive conditions, it can also result in an electrochemical action being initiated between the chromium-rich and the chromium-depleted areas and cause total failure due to destruction of the grain boundaries with resulting lack of coherency of the

TABLE I

Materials of Construction: 18–8 Stainless Steels

Type No.	Ni %	Cr %	C Max %	Mn Max %	Si Max %	P Max %	S Max %	Mo %
304	8–12	18–20	0.08	2.0	1.0	0.045	0.03	—
304L	8–12	18–20	0.03	2.0	1.0	0.045	0.03	—
316	10–14	16–18	0.08	2.0	1.0	0.045	0.03	2.0–3.0
316L	10–14	16–18	0.03	2.0	1.0	0.045	0.03	2.0–3.0