Technical News Features

✗Glycerolysis of Fats and Methyl Esters —
Status, Review and Critique[1]

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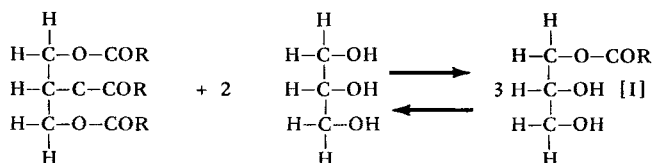
ABSTRACT

With the possible exception of catalytic hydrogenation, perhaps no unit operation within the realm of oleochemistry is as thoroughly complex as that of glycerolysis. Among the misconceptions and half-truths that prevail concerning the glycerolysis of fats are the notions that it involves a strictly random distribution of acyl groups among all of the available hydroxyl groups, that the solubility of glycerol in the fat at the reaction temperature determines the yield of monoglyceride that may be obtained, that the advantageous effects of the Law of Mass Action can be realized only when the reaction media is in ultimate homogeneity, in other words, complete mutual solubility, and, more importantly, that there is an equivalence of emulsification properties for the chief products of glycerolysis, i.e., the α- and β-monoglycerides, in both food and industrial emulsification. Numerous examples from international literature establish the limitations which prevail in temperature, agitation and use of excess of glycerol in batch glycerolysis reactions, but the practical limits for glycerolysis under *superemulsification* conditions remain to be established. The disadvantages of glycerolysis in homogeneous solvents still are insufficient to justify the use of those that are available, but the use of both pressure and gaseous catalysts such as carbon dioxide appear to offer the greatest hope for improvement in yields. Substantial energy savings may dictate the choice of methyl ester glycerolysis processing for future plants, especially those in the international sphere. Pros and cons of monoglyceride analytical methodology are evaluated.

INTRODUCTION

General Characteristics of Fat Glycerolysis

With the possible exception of catalytic hydrogenation, few, if any, reactions in the realm of oleochemistry are as complex as fat glycerolysis. To compound the confusion associated with this reaction, the chemical literature abounds with examples of inconsistencies and half-truths pertaining to it.

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Equation I is the main, overall, simplified chemical equation for fatty glycerolysis. It is simplified because it represents only the predominant monoglyceride product; it takes no account of the formation of the 2-acyl or β-monoglyceride which does occur in every reaction at every temperature, but generally in the range of 5-8% (at low temperatures) to up to about 30% (at the very highest temperatures), of the total monoglycerides formed.

Fat glycerolysis shows nature's way of distributing avail-

able acyl groups in the charge mixture more or less randomly and regularly among all of the fatlike molecules that are present. In the past, it has been assumed that such a distribution of acyl groups was governed entirely by statistical considerations; however, this is contrary to the known differences in the relative chemical reactivity of primary and secondary hydroxyl groups in both direct esterification and interchange reactions.

The reaction is "additive" in the sense that water is neither absorbed nor eliminated (as is the case with direct esterification).

The reaction is reversible when it is carried out homogeneously (or "near" homogeneously, as under conditions of *superemulsification*), and is subject to the Law of Mass Action. As a direct consequence of this, it is obvious that use of an excess of glycerol over the 2 moles theoretically required results in the displacement of the equilibrium to the right, and thus, higher total monoglycerides. This demands that the excess glycerol which remains unaltered in the crude reaction mixture must be removed.

The main difficulty in achieving practical success in fat glycerolysis is in establishing a sufficient degree of homogeneity, or mutual solubility, of the hydrophilic glycerol in the initial hydrophobic triglyceride fat or in subsequent fat-like phases. Glycerol, at room temperature, is only about 4% soluble in common fats, and perhaps a little more so, say 6%, in coconut oil. This is less than the theoretical 2 moles required to react overall, and, thus, no possibility at room temperature exists for the use of excess glycerol to force the reaction to completion. Consequently, elevated temperatures must be (and have been) used to increase the solubility of glycerol in the fat phases. Optimally, at about 250 C, the solubility of glycerol in fats (expressed as lb glycerol/100 lb fat, or %) is about 40-45% for hydrogenated cottonseed oil or hydrogenated tallow, and perhaps 65% for coconut oil. At this temperature, it is implied that the practical limits of molar excesses of glycerol are about 110% for cottonseed or tallow and 142% for coconut oil.

If the excess glycerol customarily used in catalyzed fat glycerolysis reactions is removed, as it usually must be by some means, the Law of Mass Action dictates that the reaction will reverse itself. For this reason, catalysts are usually, but not exclusively, neutralized in order to take advantage of the substantially lower rates of reaction, both forward and backward, of the uncatalyzed system. Thus, at the finish of the glycerolysis at high temperature, the catalyst is first completely neutralized, and the reaction is cooled, during which time the solubility of the excess glycerol in the monoglyceride-rich medium is decreased to such an extent that some of this excess is thrown out of solution and separates heterogeneously into a heavier, lower layer. Then, in complete accord with the Law of Mass Action, tri- and diglycerides are regenerated as the heterogeneous mixture "reverts," fairly rapidly at very high temperatures. However, the rate of reversion is so much slower than in the case of

the catalyzed system that usually the excess glycerol can be removed fast enough and the reaction can be substantially cooled before significant reversion can occur. If the catalyst is not neutralized or is incompletely neutralized, reversion can occur to the extent of about 30%; with carefully neutralized crudes and rapid cooling, it can be satisfactorily limited to a few points when it is carefully and rapidly cooled to a temperature at which the reversion velocity is essentially nil. Thus, the catalyst neutralization plus the cooling and removal of the glycerol excess are the key steps in conventional batch fat glycerolyses and must be done with care and speed. It should be pointed out again that complete neutralization of the catalyst at the range 250-260 C does not automatically guarantee that reversion will not occur unless cooling and glycerol removal are rapid. The rate of reversion of uncatalyzed systems at 255-260 C is still significant.

As indicated, the reaction is catalyzed, preferably by alkaline catalysts like NaOH, KOH, Ca(OH)$_2$ (hydrated lime for better colored crudes) or with CaO, even SrO, or the sodium salts of lower aliphatic alcohols such as methanol, ethanol, tert-butanol, and also by acids, but much more slowly than with alkalies. Certain metals such as Na, K or Sn (powder) have also been used as catalysts. There is much credence to the notion that alkaline catalysts function as emulsifiers, since alkalies generate small quantities of soap from the free fatty acids present in all fats, and in view of the known emulsifying performance of soap with glycerol/fat mixtures. Invariably, emulsification of the media aids reactivity as the two otherwise immiscible (or insoluble) reactants are brought into more intimate contact with one another. In most instances, the line between the terms "catalyst" and "emulsifier" in fat glycerolysis is quite vague and indefinite. The action of practically all catalysts could be attributed, at least in part, to that of emulsification. In recent interchange studies, investigators have attempted to differentiate between the action of catalysts such as metallic sodium or potassium or their hydrides and emulsifiers such as sodium, potassium or lithium oleates. The need to specify the exact function of this reaction promoter, i.e., whether true catalyst ·or emulsifier, is somewhat meaningless, and reference to the use of either or both is now generally represented by the inclusive term "catalyst."

It is obvious that in order to achieve some useful degree of reaction velocity and ultimate completeness, optimally elevated temperatures usually are used; thus, the reaction as it is commercially practiced has a relatively high thermal energy demand. The tendency in the last 20 years has been to operate at increasingly higher temperatures, consistent with attainment of greater solubility of the reactants. Early work generally involved 180-200 C. Later studies ranged from 200-220 C and today the range is mainly 220-260 C, product use and performance permitting. This is a high reaction BTU demand necessitating the need for over 250,400 BTU/1,000 lb charge for heating of conventional 69%/31% fat/glycerol charge mixtures.

Equation I suggests a trimolecular reaction; this is false and misleading. The reaction occurs stepwise in a series of two steps represented by two successive equations with different reaction rates. Glycerol and fat react initially to yield the separate diglyceride isomers, the 1,3- and 1,2-diglycerides, and these, through second interchange, generate the 1- or 2-monoglycerides.

Finally, the simplified equation illustrates nothing of a further degree of complexity in the reaction that depends on the stability of the two monoglyceride isomers formed. This appears to be primarily a temperature-dependent equilibrium between α- and β-monoglycerides, which, to some extent, overrides the need to consider the relative reactivities of primary and secondary hydroxyl groups in the reaction.

For example, at 100 C, the equilibrium mixture of most fat monoglycerides is about 90% of α-monoglyceride (1). The relative β-isomer content is increased at higher temperatures. As a consequence of this temperature-dependent equilibrium, it is apparent and demonstrable that β-isomer interchanges and thus decreases during cooling of reaction mixtures, with the corresponding increase of the α-monoglyceride. If the cooling operation is carried through the point of solidification, the isomerization is "frozen," with the rate of β- to α-monoglyceride isomerization very slow but still perceptible in the solid state. It should also be noted that the equilibrium of α- and β-monoglycerides is subject to the influence of high acidity in accord with the observation that monoglyceride mixtures can be isomerized completely to the α-isomer in the presence of perchloric acid (2).

Half-Truths and Inconsistencies on Fat Glycerolysis

There are four concepts prevalent on glycerolysis which should be dispelled because they are half-truths and inconsistent with some recent facts. The first is the misleading assumption that a statistical distribution of acyl groups occurs between primary and secondary hydroxyl groups, an assumption that has given rise to useful generalizations that are approximately true in some, but not all, examples of fat glycerolysis. The assumption is contrary to the known differences in reactivity between primary and secondary hydroxyl groups in both direct esterification and in ester interchange (1).

A second half-truth is that the solubility of glycerol in the fat at the reaction temperature determines the yield of monoglyceride that can be obtained. Although it has been useful for over three decades (3), this concept is now invalid. It does not explain the high yields of monoglyceride obtained in reactions under conditions of superemulsification, where the fat-like phase and glycerol are still heterogeneous.

In conventional fat glycerolysis, the composition of the reaction mixture gradually changes as reaction progresses, i.e., both 1- and 2-monoglyceride content increases as triglyceride content diminishes, and the solubility of the glycerol in the near-equilibrium mixture is, presumably, much higher than it is in the triglyceride starting material. Thus, conclusions based on the solubility of the starting materials are not valid when they are used to predict the optimal ratio of miscible reactants for any conversion to monoglycerides. The determination of the solubility of glycerol in fats without interchange catalysts present is not possible at temperatures above about 200 C since uncatalyzed interchange has already commended at those temperatures.

A third inconsistency is the notion that interchange occurs only in homogeneous medium under conditions of complete miscibility (or solubility) in accord with the Law of Mass Action. This is inconsistent with recent observations that in some heterogeneous media, e.g., under certain conditions of superemulsification, conversions in high yield are achieved at temperatures which are too low to account for the glycerol in fat solubility required for the Law of Mass Action to operate.

Finally, a fourth misconception is the tacit assumption, prevalent in the food industry primarily, that there is an equivalence of emulsification properties of the chief products of the glycerolysis of fats, i.e., the α- and the β-monoglycerides in both food and industrial applications. In the operation of baking bread, for example, neither all α- or all β-monoglyceride additives can ever be present at any time. The baking temperature establishes the equilibrium mixture of isomers actually present. The emulsification properties and the extent of bread "softening" (at room temperature) are all average effects of the particular ratio of isomers present at the temperatures used. This does not require that the

performance of each isomer be equivalent. Where monoglycerides are used in industrial emulsification under conditions of high acidity or alkalinity there is no reason to assume that α-monoglycerides (with one primary and one secondary hydroxyl) are equivalent in hydrophilic character and emulsification properties to β-monoglycerides (with two primary and no secondary hydroxyls).

Optimal Conditions for Commerical Production by Batch Methods

Conventional batch-type fat glycerolyses generally involve (a) optimal use of heat and agitation to maximize solubility of glycerol in the fatty phases, (b) use of excess glycerol over theoretical 2 moles required, and removal of excess at the end of the glycerolysis reaction, (c) use of a catalyst/emulsifier system without purposeful addition of soap as-is, and (d) catalyst neutralization (not exclusively in all the known processes) after completion of glycerolysis and before glycerol excess removal and cooling.

Temperature

The practical temperature limit for fat glycerolysis is 260 C for industrial products and depends on the pyrolytic stability of fat, diglyceride, monoglyceride and glycerol itself. In food monoglyceride production, the temperature is usually limited to 255 C since taste, aroma, flavor and color of the products begin to deteriorate if it is prepared at temperatures higher than this. Many individuals on food product taste panels detect a characteristic "burnt" taste for products containing mono- and diglycerides prepared at very high temperatures.

Glycerol is pyrolytically converted to undesirable acrolein at temperatures above 255 C in the presence of acidic catalysts (4) (rarely used in commercial monoglyceride production), but the formation of acrolein is not usually encountered with alkaline catalysts below 260 C. The influence of air at any temperature above 200 C is especially undesirable with development of color, and increase in acid and peroxide values observed. Fat glycerolyses are blanketed with nitrogen gas (carbon dioxide is avoided with alkaline catalysts), otherwise oxidation affords taste and color problems.

Agitation

The optimal agitation required in fat glycerolysis depends on whether an emulsifier is used. In conventional type glycerolyses soap is not generally used when the product monoglycerides are intended for food purposes. Optimal turbine type agitation is required and sufficient torque is necessary to throw a heavy glycerol layer up, into, and "through" a lighter triglyceride layer in the initial part of the reaction. For the remainder of the cycle it is specified that "good and efficient" agitation be used. Usually, no adverse effects are noted if the crude is agitated to the point of incipient emulsification, if layer separation is not required later. Frequently, agitation is continued during the cooling and excess glycerol removal steps if vacuum distillation is used. The limitations of agitation are only those of mechanical design of turbine and reactor and the cost of power. In the case of superemulsification glycerolyses, the cost of energy required to reduce the average size of the emulsion particles is particularly limiting.

Molar Excess of Glycerol and Time Cycle

The practical limit for the use of excess glycerol in the charge in conventional glycerolyses is about 110% for hydrogenated tallow and cottonseed oils and about 140% for coconut oil, as dictated by the optimal solubility of glycerol in the fats at 260 C. This corresponds to a solubility of glycerol in fats (expressed as lb glycerol/100 lb fat) for hydro-

genated tallow and cottonseed oil of about 45%, and 65% for coconut oil. Generally, cycle times are in the neighborhood of 4 hr.

Use of Catalysts—Advantages and Disadvantages

For industrial fat glycerolyses NaOH or KOH are the preferred catalysts because the rate of interchange is high and the catalysts are inexpensive. Occasionally, sodium salts such as $NaOC_2H_5$ or $NaOC_4H_9$-t are worth the slightly higher cost in promoting a faster rate. For food monoglycerides, hydrated lime, $Ca(OH)_2$, is preferred because of low color development in the final product. Catalysts must be used in order that the reaction rate is within practical limits of about 4 hr cycle time. Depending on the specific catalysts used, between 0.05-0.20% (based on the weight of fat charged) are used; hydrated lime catalyst levels are 0.06-0.10%. The reaction between a fat and glycerol will take place without a catalyst present but the rate is reasonably rapid only near 287 C, or prohibitively too high for practical commercial operations.

Although catalysts must be used, some operating disadvantages accrue through their use. Catalysts cannot be left unneutralized or unremoved in monoglycerides because they cause reversion, and furthermore, contribute, in the case of food emulsifiers, to problems of soapy taste, color stability, and occasionally, when the product is used at higher temperature, to foaming problems. An important reason for neutralizing catalysts in hot glycerolysis reaction crudes prior to cooling and before glycerol removal by vacuum distillation is that, otherwise, the crude will almost certainly revert. With catalyst neutralization the reversion rate is substantially lowered.

The usual catalyst neutralization technique is with phosphoric acid, followed by adsorption of the neutralization products, the calcium, sodium or potassium phosphates, with clays. There is an attendant fatty monoglyceride loss in any clay adsorption and filtration treatment. In the case of hydrated lime neutralization there are further difficulties. The catalyst is neutralized precisely in accord with the chemical equation:

$$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O.$$
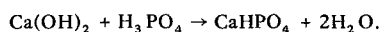
At the higher temperatures used in rapid glycerolyses, the byproduct calcium hydrogen phosphate is converted by heat to glasslike, polymeric metaphosphates which are prone to cause filtration problems. Quick cool-downs with lime catalysts are critical to minimize these problems.

Patented Batch and Continuous Fat Glycerolysis Processing

Table I summarizes the existing patented technology for both batch (Roman print) and continous (italics) glycerolysis processing.

Grun, in 1924, an Austrian residing in Czechoslovakia, proposed monoglyceride production by fat glycerolysis as the first step in the formation of a "synthetic butter." In an American patent assigned to himself, he taught that fats such as palm oil and tallow could be interchanged with glycerol, catalyzed with tin metal, and form mono- and diglyceride mixtures which on direct esterification with low molecular weight fatty acids would yield acceptable triglyceride synthetic butters. Apparently, this was the first patented glycerolysis.

The two Gooding and Valteich patents, assigned to Best Foods, Inc., are innovative methods designed to remove soaps obtained from relatively high levels of alkaline catalysts such as $NaHCO_3$ and Na_2CO_3 in peanut oil glycerolysis reactions. U.S. Patent 2,197,339 describes how the crude soap/ester mixture may be reacted with selected chlorohydrins like glycerol chlorohydrin, ethylene chlorohydrin or with other chloro compounds with the formation

TABLE I

Patented Nonsolvent Fat Glycerolysis Processes[a]

Year	Patentee and (assignee)	Patent ref.
1924	A. Grun (to himself)	U.S. Pat. 1,505,560
1940	C.M. Gooding and H.W. Valteich (to Best Foods, Inc.)	U.S. Pats. 2,197,339-340
	A. Edeler and A.S. Richardson (to Procter & Gamble Co.)	U.S. Pats. 2,206,167-8
1945	*J. Arrowsmith and J. Ross* (to Colgate-Palmolive-Peet Co.)	U.S. Pat. 2,383,581
1949	*H. Ittner* (to Colgate-Palmolive-Peet Co.)	U.S. Pat. 2,474,740
	H.D. Allen and J.D. Malkemus	U.S. Pat. 2,478,354
1950	A.C. Bell and W.G. Alsop (to Colgate-Palmolive-Peet Co.)	U.S. Pat. 2,496,328
1952	*N.H. Kuhrt and Distillation Products Industries* (to Eastman Kodak)	British Pat. 682,625
1953	*N.H. Kuhrt* (to Eastman Kodak Co.)	U.S. Pats. 2,634,278-9
1959	G.E. Woods (to Atlas Powder Co.)	U.S. Pat. 2,909,540
	H. Birnbaum (to Hachmeister, Inc.)	U.S. Pat. 2,875,221
1962	R.K. Kochar and R.K. Bhatnagar (to Council of Scientific and Industrial Research, India)	Indian Pat. 71,979
1963	H. Birnbaum and J. Lederer (to Hachmeister, Inc.)	U.S. Pat. 3,102,129
	R.W. Giddings and A.C. Davies (to Lever Bros. Co.)	U.S. Pat. 3,095,431
	S.S. Chang and L. Wiedermann (to Swift and Co.)	U.S. Pat. 3,079,412
	W.G. Alsop and I.J. Krems (to Colgate-Palmolive Co.)	U.S. Pat. 3,083,216
1967	R.R. Allen and R.L. Campbell, Jr. (to Anderson-Clayton and Co.)	U.S. Pat. 3,313,834
	N.I. Gel'perin and I.N. Gula (no assignment)	USSR Pat. 193,485
1970	M. Bea-Salvia (no assignment)	Spanish Pat. 383,780

[a]Batch processes are in Roman type; continuous processes are in italics.

of NaCl and an ester, both of which were left in the product. In U.S. Patent 2,197,340, glycerol and H_2SO_4 are added to the soap/ester crude to form fatty acid and Na_2SO_4, the former esterifies the glycerol to produce mono- and diglycerides. Here, too, the entire byproducts were left in the product ester. Note the unique formation of additional monoglyceride in the use of glycerol chlorohydrin as a reactant.

The Procter & Gamble Company patents of Edeler and Richardson are two processes dealing with the use of soaps or alcoholates in glycerolysis. U.S. Patent 2,206,167 deals "with soap-catalyzed" glycerolyses at 150-206 C, whereas U.S. Patent 2,206,168 relates to the use of either soaps or alcoholates like $NaOC_2H_5$ or KOC_2H_5 at 90-175 C with a N_2 sparge or under slight vacuum to ostensibly remove water traces.

The *Arrowsmith and Ross* patent, assigned to Colgate-Palmolive-Peet Co., relates to the glycerolysis of fats at 150-250 C, neutralization of the catalyst, and separation of the glycerol excess by vacuum distillation, followed by separation of the monoglyceride by distillation. Alternately, glycerol may be first separated by gravity layer separation and the monoglyceride then vacuum distilled.

The *Ittner* and the Allen and Malkemus patents, assigned to Colgate-Palmolive-Peet Co., are innovations in which wet glycerol is used in countercurrent continuous processes of glycerolysis. U.S. Patent 2,474,740 specifies glycerol containing from 5-10% of water used at 240 C under pressure of 670 psig with the final product from coconut oil said to contain 56% monoglycerides and 12.7% free fatty acids. U.S. Patent 2,478,354 is essentially a two-step process in-

volving a pressure reaction at 200-250 C near 45 psig, then a depressurizing and removal of water. It may be operated batch or continuously. The product was claimed to be 92% total monoglycerides with 1.2% free fatty acids.

The Bell and Alsop patent, assigned to Colgate-Palmolive-Peet Co., describes an alkali-catalyzed glycerolysis process using glycerol at 4-10 moles/mole of fat in minute dispersion at 240-260 C, extremely rapid cooling of the finished crude to 100 C without catalyst neutralization and layer separation. The crude ester layer corresponds to about 50% monoglycerides.

The *Kuhrt* patents, assigned to Eastman Kodak Company, now Eastman Chemical Products, Inc., describes a continous process for "distilled" (90+%) monoglyceride production operated by Eastman at Rochester, New York, for over 25 years with essentially little domestic competition. British Patent 682,625 describes how unneutralized glycerolysis catalysts can be separated by means of vacuum distillation from a thin film of crude to give unaltered partial glycerol esters as distillates. U.S. Patent 2,634,278 details the three-cycle operation whereby molecular distillation is used successively to separate glycerol and the high monoglyceride products. In an example, 1 mole of soybean oil with 2.3 moles of glycerol and 0.1% by weight SrO is preheated to 225-230 C, then reacted in a pot reactor for 20 min at 250-260 C under constant agitation venting off water. The mixture is cooled rapidly to 100 C, the glycerol layer is withdrawn after 5 min, then glycerol is stripped off the upper layer in a high vacuum centrifugal still at 100 C and 100 μ to remove more of the excess. The distillation residue is passed to a second still and, at 20 μ and 120 C

rotor temperature, the remainder of the glycerol and a small amount of monoglyceride are removed. The undistilled residue is then subjected to a third distillation at 3 μ and a rotor temperature of 170 C and 30% of the charge is distilled off as pure monoglyceride containing less than 1% glycerol. The distillation residue is then subjected to a molecular distillation at 3 μ and 210 C whereby any monoglyceride is removed and sent to the previous stage of centrifugal distillation. The final distillation residue containing diglycerides, triglycerides, and active catalyst is combined with unreacted glycerol cuts, replenished with more oil and glycerol and recycled. U.S. Patent 2,634,729 is similar to British Patent 682,625.

The Woods patent, assigned to Atlas Powder Co., now ICI Americas, Inc., describes a method of minimizing reversion involving cooling the finished crude rapidly by distilling off added glycerol without added heat. Hydrogenated edible tallow afforded a total monoglyceride yield of 66% with a free glycerol content of less than 2% by this process.

The *Birnbaum* and *Birnbaum and Lederer* patents, assigned to Hachmeister, Inc., represent technology used by the defunct Hachmeister operation at its Neville Island plant in the Ohio River just north of Pittsburgh, PA. U.S. Patent 2,875,221 represents a continuous NaOH- or KOH-catalyzed glycerolysis process using "near-stoichiometric" quantities of glycerol in which reaction is carried out in the presence of 5-10% of a preformed, about 50% monoglyceride material, first at 246-274 C, then in thin-film in a Votator at 246-274 C for about 30 min (after which 10% of the crude is recycled), with neutralization of the catalyst to form MH_2PO_4 salts, cooling to 93-177 C, filtration of the salts, and removal of excess glycerol by vacuum stripping. With lard as the fat, yields of α-monoglycerides prepared by this process are: 66.2%, as described using 10% high monoglyceride diluent; 63.9%, with the use of only 5% high monoglyceride diluent; 54.2%, with omission of the recycle step; and 41.7%, with omission of diluent entirely.

U.S. Patent 3,102,129 represents the extension of a modified (without the use of preformed monoglyceride as a diluent) process with the incorporation of molecular distillation for "distilled" (90%) monoglycerides.

The Giddings and Davies patent, assigned to Lever Bros. Co., is a three-stage, continuous, catalyzed glycerolysis process in which the reactants are mixed and heated, with ample air-free blanketing, then reacted for a short time at 250-270 C, then quickly cooled without catalyst neutralization or glycerol removal. The products from this process are "40%-type" monoglycerides and have glycerol contents of 4-9%.

The *Chang and Wiedermann* patent, assigned to Swift and Co., is a continuous countercurrent, packed-tube catalyzed process in which "homogenized" fat or oil containing a little glycerol is fed at the bottom of a glass helices-packed column and glycerol and NaOH at the top, held at 220-250

C for a 2-3-min residence time. Product overflows at the top, and without substantial cooling, is neutralized with ion-exchange resin (such as Permutite G) to give 70% (total?) monoglycerides. As far as is known, this process was never commercialized.

The Alsop and Krems patent, assigned to Colgate-Palmolive Co., teaches that both fats and partially esterified fats may be interchanged uncatalyzed at temperatures above 270 C for short time periods to give, upon cooling to 100 C, two layers, separable by centrifuging. The upper layer is stripped of excess glycerol by distillation at 100-140 C at 1 mm Hg, and the glycerol-free product was said to consist of 90% monoglyceride and 10% diglyceride.

The *Allen and Campbell* patent, assigned to Anderson-Clayton & Co., is a continuous, catalyzed glycerolysis process which involves operation at about 45 psig and 249 C, withdrawing a part of the crude continuously, stripping off glycerol, cooling to about 176 C, neutralizing the catalyst, followed by filtration removal of the salts. A product from soybean oil contained 58.2% α-monoglyceride when prepared in accord with this process.

The Russian patent details a soap-"catalyzed" glycerolysis carried out at 200-210 C, on which little further data are available.

Finally, the Bea-Salvia Spanish patent is apparently concerned with the development of a cosmetic partial ester from coconut oil by a glycerolysis process using, as *Chemical Abstracts* states, "a base alkali metal catalyst."

Solvent Batch Fat Glycerolysis

One obvious way to create an environment in which the Law of Mass Action may operate satisfactorily is to dissolve both glycerol and fat in a mutual solvent. Table II summarizes almost all the solvent fat glycerolyses that have been studied, reported or patented. Although the work is not extensive, good to excellent yields are observed; the limitations and difficulties are the result of entirely different factors.

There are very few solvents available that offer simultaneous solubility of fats and glycerol; 1,4-dioxane is one. It was suggested by Richardson and Eckey and Richardson, who determined that it was also useful in direct esterifications for high monoglyceride product. Unfortunately, it has been found (5,6) that 1,4-dioxane is carcinogenic to rats, and this fact almost completely eliminates it for use in fat glycerolyses for food monoglycerides; industrial utilization also is considered unlikely.

Cresols and phenol were patented by Hilditch and Rigg for use as solvents in the direct esterification of glycerol with fatty acids for high monoglyceride esters; presumably they could function also as fat glycerolysis solvents were it not for their relatively high cost, toxicity, and the necessity for their complete removal from the products because of their obnoxious and persistent odors.

TABLE II

Solvent Glycerolysis Processing

Year	Authors or patentees	Ref.	Solvents
1937	T.P. Hilditch and J.G. Rigg	U.S. Pat. 2,073,797	Phenol or cresols
1941	A.S. Richardson (Procter & Gamble Co.)	U.S. Pat. 2,251,692	1,4-Dioxane
	A.S. Richardson and E.W. Eckey (Procter & Gamble Co.)	U.S. Pat. 2,251,693	1,4-Dioxane
1957	R.S. McKinney and L.A. Goldblatt	JAOCS 34:585 (1957)	Pyridine (tung oil)
1967	C. Franzke et al.	Nahrung 11:639 (1967)	Pyridine (sunflower oil)

Pyridine is probably the last of the very few solvents that offers some potential for use. Franzke et al. conclusively demonstrated the advantages of this solvent for high yields of monoglycerides at relatively low temperatures. Sunflower oil, heated at 115-120 C for 3 hr using 10 parts by wt of oil and 20 parts glycerol with 0.3 parts NaHCO₃ as catalyst in excess pyridine afforded, after removal of the excess glycerol at the completion of the reaction, a 75% α-monoglyceride or 83% total monoglyceride yield. The reaction charge corresponded to the use of 9.37 moles of glycerol/mole of oil, or 370% molar excess. The same ratio of reactants at 200 C without a solvent yielded 52% α-monoglyceride and 58% total monoglycerides. At 200 C, glycerol is only soluble to the extent of about 23 parts/100 parts by wt of common fats. Thus, the nonsolvent example illustrates that although 9.37 moles of glycerol/mol of fat was charged to the reactor, only about 2.16 moles was solubilized in homogeneous medium, corresponding to the use of only about 8% molar excess of glycerol.

McKinney and Goldblatt also used pyridine for tung oil glycerolysis, but their high reported yields could not be repeated by other workers, who presumably encountered severe reversion in attempting to duplicate this work. Solvents offer the prospects of high yields at relatively low temperatures, but disadvantages in their handling, toxicity, noxious odors, and the need to remove them completely from the products explain why limited effort has been directed to solvent glycerolysis. Furthermore, solvent use severely restricts production capacity of the reactor and demands solvent recovery equipment and solvent storage systems. Obviously, low molecular weight alcohols and esters cannot be used for fat glycerolyses, but if an inexpensive, low-boiling, innocuous and nontoxic, inert solvent possessing the required mutual solubility for glycerol and fats could be found, it might be used satisfactorily.

Glycerolysis under Emulsification and Superemulsification

It has been appreciated for over 40 years that soap is an ex-

cellent emulsifier for fat glycerolyses in that it permits the use of higher effective glycerol concentrations not necessarily in the soluble state but rather in a state where more intimate contact and reactivity of glycerol and fat or partial fat are vastly promoted.

Table III illustrates the advantageous effect of ordinary soap as an emulsifier in coconut oil glycerolyses. Edeler and Richardson, in two U.S. patents assigned to Procter & Gamble Co., showed that with 1.4-2.0% commercial soap (based on glycerol and coconut oil charge) monoglyceride yields could be nearly 97%. In the first example, the S.V. analysis was on the upper layer after removal from the lower glycerol layer but uncorrected for dissolved glycerol and soap. In the second example, S.V. analysis was on the upper layer after removal from the lower layer, and washing with water to remove dissolved glycerol and soap. The second example, therefore, is the more accurate and reliable figure. Note the 68% yield afforded in one typical coconut oil glycerolysis at 250 C without addition of soap.

Coconut oil appears to respond to common soap in glycerolysis more effectively than do the common fats such as hydrogenated tallow, hydrogenated soybean or cottonseed oils, where the yield results are variously improved only to the extent of 10-30% above those from comparable nonsoap reactions. The reasons are somewhat obscure.

For food monoglyceride production, soap as an emulsifier has not been used for various reasons. The removal of soap by clay absorption and filtration is accompanied by a relatively high monoglyceride absorption loss, and small traces of soap are objectionable in food additives because of their foaming and taste effects. If soaps are acidulated to free fatty acids, metallic salts must be first removed by water washing and the product dried. Free fatty acids are also objectionable because of their taste and flavor effects, and the removal of them by refining, unlike that for fats, is ineffective.

Table IV presents comparative data on hydrogenated cottonseed oil glycerolysis under four distinct conditions of

TABLE III

Effect of Soap as Emulsifier in Coconut Oil Glycerolysis[a]

| | Charge | | | | | |
G₃/CO	Wt % G₃ on G₃ + CO	Wt % soap G₃ + CO	Temp (C)	Time (hr)	S.V. upper layer	Yield CO Monos (%)
0.4333	30.23	1.4	175	2	186.5	almost 100
1.000	50	2.0	200	2	197	96.9
0.6000	37.5	none	250	3	205	68

[a]Source: Edeler and Richardson, U.S. Pats. 2,206,167-8 (July 2, 1940).

TABLE IV

Comparison of Approxiamte Total Monoglyceride Yields at 255 C for Hydrogenated Cottonseed Oil under Four Conditions of Nonhomogeneous Reaction Media

Condition	Ave. size of particles, cm (μ)	Appearance of media	Equipment used	Approximate total, monoglyceride yield, % 255 C)
Fine dispersion	10⁻³ (10)	Drab, opaque, fine dispersion	Propeller stirrer	61
Emulsion, ordinary	10⁻⁴ (1)	Milky, opaque	Turbine (with emulsifier)	65 (coconut ca. 97)
Emulsion, high, near "superemulsion"	10⁻⁵ (1 - 0.1)	Blue-white, opaque	Homogenizer or colloid mill	ca. 80
Superemulsification	10⁻⁵ (0.05 or smaller) to 10⁻⁶	Transparent, slight bluish cast	Sonic energy	95-?

dispersion, emulsification and superemulsification, assuming the reaction is conducted at 255 C. In the dispersed state, we observe the conventional results in batch reactions that are typical of most of the reactions that have been studied. The emulsified state is typical of soap-emulsified reactions or those in which homogenizers are used. Further decreases in average particle size to the 1-0.1 μ range are rewarding if we can afford the cost of the energy required to accomplish it. This area range apparently is just at the beginning of the superemulsification range. Finally, at the range of average particle size of 0.05 μ or lower, considered as the superemulsification state, is still heterogeneous (although hardly) but in which, apparently, the Law of Mass Action operates advantageously despite the fact that the two liquids are not mutually soluble in one another. Any new mechanical developments in sonic energy equipment or other devices which result in a decrease in the present cost of generating the state of superemulsification, of course, would be highly desirable. New developments in this area are virtually certain as are those in the realm of sucrose/methyl ester interchange for sugar esters suited for food and cosmetic use.

CO₂-Catalyzed Pressure Glycerolysis

Table V presents data on the CO_2-catalyzed pressure glycerolysis of some fats and oils. Despite the fact that this work was initiated about 18 years ago, the processing is relatively little known and appreciated. Perhaps this may be due to the fact that *Chemical Abstracts* (58:688a [1964]), in summarizing this Indian patent, did not include the information given on line 4 of Table V.

TABLE V
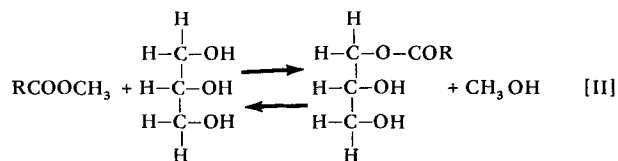
CO₂-Catalyzed Pressure Glycerolysis[a]

Oil	Pressure	Yield mono
Castor	100-150	82.5
Coconut	100-150	74.6
Peanut	100-150	73
Castor	700-750	91

[a]Source: R.K. Kochar and R.K. Bhatnagar, Indian Pat. 71,979 (1962).

To say that gaseous carbon doxide "catalyzes" a fat glycerolysis would be presumptive were it not for the fact that when air or nitrogen gas replaces the carbon dioxide under the same conditions, the reaction is not appreciably catalyzed. The patent claims that "aqueous carbon dioxide" is the catalyst, implying that water is included in the charge.

Obviously, this process could have so many operating advantages over conventional alkali-catalyzed fat glycerolyses that it is surprising that greater use has not been made of it. Catalyst removal (not neutralization) consists of a depressurizing step, presumably followed by a nitrogen gas sparge to remove the last traces, no neutralization, no salt formation, no filtrations with consequent loss of absorbed monoglyceride oil, and no filtration-slowing calcium metaphosphates (in the case of lime catalysts). Presumably, reversion is minimized to the extent that the reaction can be rapidly cooled. The surprisingly high α-monoglyceride yields could eliminate expensive molecular distillation for future world 90% monoglyceride production.

Glycerolysis of Methyl Esters

$$RCOOCH_3 + \begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H \end{array} \rightleftharpoons \begin{array}{c} H \\ | \\ H-C-O-COR \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H \end{array} + CH_3OH \qquad [II]$$

Glycerolysis of methyl esters offers perhaps the greatest potential for future utilization for 40, 60 and 90% monoglycerides. The methyl ester glycerolysis chemical equation II is reversible and offers the advantage for the employment of the "push-pull" effect in displacing the equilibrium toward the right, or to higher monoglyceride yields. The use of excess glycerol and the simultaneous removal of by-product methanol by vacuum is highly effective for this purpose. (Fat glycerolysis, in contrast, is only "push" effective; although it responds to the use of excess glycerol in the charge, it does not respond to application of vacuum, except in some processes during removal of traces of water.) Second, little necessity thus far has been evidenced for emulsification in order to bring the reactants into more intimate contact; however, in future work, it is quite probable that advances in this respect will be made because methyl esters as a class are far less hydrophobic than triglyceride fats. Finally, there is considerable thermal energy advantage to the glycerolysis of methyl esters over fat glycerolysis, i.e., about 120-200 C for the methyl esters compared to about 260 C for fat glycerolysis; also, methyl esters are derived from fats by energy-conserving fat methanolysis reactions (7). Furthermore, and perhaps more important for future sophisticated industrial monoglyceride products, methyl ester use provides the opportunity to tailor-make the monoglyceride end-product to the exact end-use requirement (methyl esters are easier to separate by fractional distillation than are fatty acids) whereas the use of fat glycerolysis affords only the distribution of acyl groups in the product that naturally occur in natural fats and oils.

It is little wonder that methyl (or ethyl) ester interchange reactions are already being applied for salad oil production in Israel (8), and that methyl esters are being investigated for anhydrous soap production in other parts of the world. Can monoglyceride production be too far behind?

A practical example of methyl ester glycerolysis is the Japanese work (9). The methyl esters of safflower oil, tall oil, rice bran oil, sperm oil and palmitic acid have been converted into 1-monoglycerides assaying 50.6-54.9% using 1 mole of methyl ester to 1.5-4 moles of glycerol with 0.1% KOH catalyst (based on the weight of methyl ester) at 215-220 C for only 25-30 min and moving methanol by distillation.

Status of Analytical Methodology

In the past, quality control analyses for all types of monoglyceride products have been based on the method of Mehlenbacher (10). This method is an official method of the American Oil Chemists' Society (Cd 11-57) and of the Association of Official Analytical Chemists (AOAC 28.139). It is a periodic acid oxidation technique including iodometry which is specific for the *vicinal* or 1,2-dihydroxy groups of α-monoglycerides and those of any glycerol that may be present, but not the 1,3-dihydroxy groups of any β-monoglycerides (which are always present to some extent). The method satisfactorily differentiates between glycerol content and gives an accurate figure for any α-monoglyceride content, presumably reflecting the composition at the laboratory temperature at which the titrations are accomplished.

It is tacitly assumed that the α/β-monoglyceride equilibrium mixture has had sufficient time to equilibrate at the laboratory temperature, but this may not be the case in those instances where analyses are determined rapidly from hot reaction crudes at or near 260 C. Since this has been the standard direct method for analysis for the past 21 years, the specification sheets for American producers of all types of monoglycerides, including 40, 60 and 90% types, have included α-monoglyceride content. The bulk of the huge American production over the years has primarily been based on α-monoglyceride as a reliable, direct analytical measurement.

In the past, if the laboratory quality control analyst wished to know the "total" monoglyceride of a product because, for example, the particular product was to be sold in the Orient or in parts of Europe, he would first determine the α-content by the standard method and then resort to the use of a conversion factor to obtain the total monoglyceride, expressing the figure at room temperature. The unofficial conversion factors used in domestic production ranged from 1.05 to 1.088, which corresponds to β-monoglyceride in the range 5-8% of the total monoglycerides. Since these factors were obtained from studies on a variety of common fats at several near-room temperatures, they were admittedly only approximate, but they were used at a reasonable degree of satisfaction for many years with common fats.

A suggestion has been made (2) that total monoglycerides may be determined as an adjunct to the standard periodate method as a direct method of analysis. It has been established that perchloric acid isomerizes α- and β-monomixtures to α-isomer rapidly and completely. If this could be incorporated into the method on another aliquot sample, the method could conceivably serve for both α- and total monoglyceride content in the presence of glycerol.

Total monoglycerides, as well as di- and triglycerides can also be determined by silica gel column chromatography using AOAC method (1980) 28.133-28.138 for monoglyceride concentrates and 28.148-18.153 for shortening. Wood et al. (11) efficiently separated 1- and 2-monoglycerides as trimethylsilyl ether derivatives on packed and large bore capillary columns of diethylene glycol succinate polyester (DEGS) and Apiezon L. Finally, a micromolar determination of 1,2-diols has been accomplished (12) by the use of atomic absorption spectrophotometry as the end-determination and might be applied to the detection of small quantities of monoglycerides in food products. The iodate formed in the oxidation of adjacent hydroxyl groups by periodic acid is separated by precipitation as silver iodate. The silver iodate is dissolved in ammonium hydroxide and the resultant solution is analyzed for silver content by means of atomic absorption spectrophotometry.

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