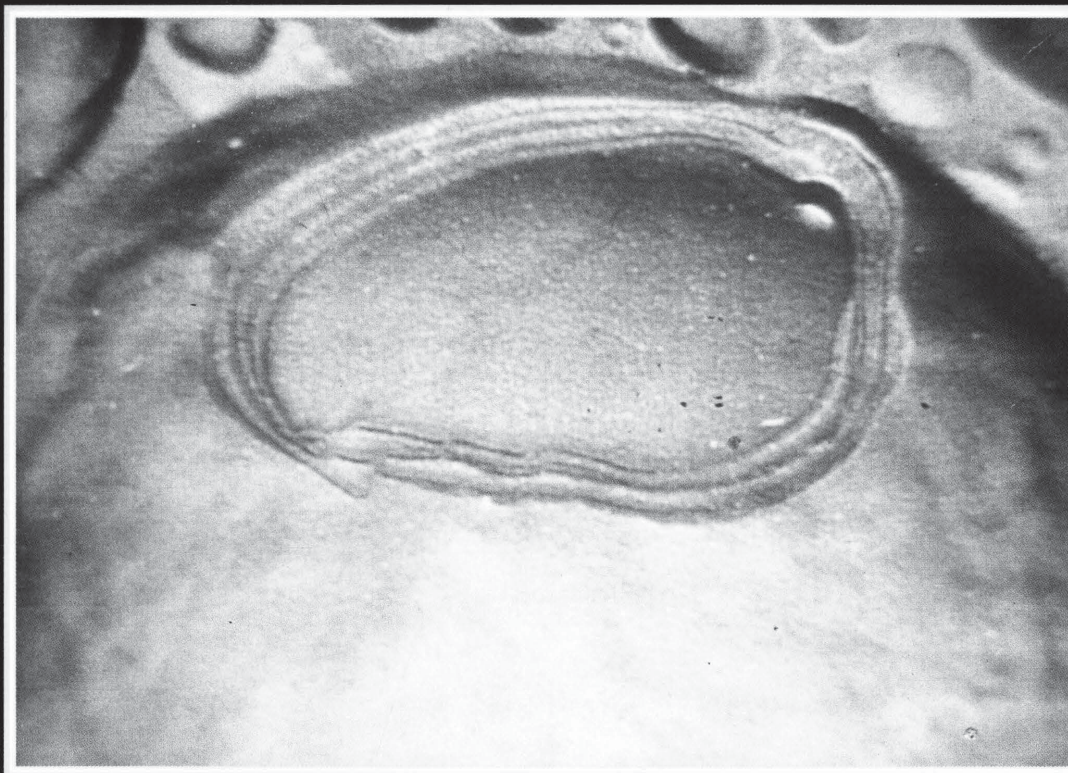


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International News on
Oils and Related Materials
The American Oil Chemists' Society

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Liposomes in personal care products

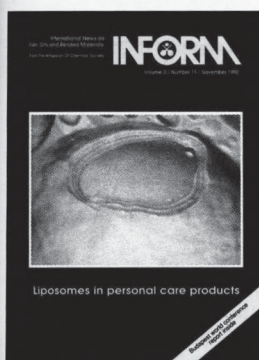
Budapest world conference
report inside

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International News on Fats, Oils and Related Materials



The cover photograph provided by IGI Inc. is an electron micrograph, using the freeze-fracture technique, of a Novasome lipid vesicle to demonstrate the multiple bilayer membranes surrounding a large central core. A look at the use of liposomes in personal care products begins on page 1172.

Photo and figure credits:
Page 1172, electron micrograph of a liposome, courtesy of H. Ping Ting-Beall of the Department of Mechanical Engineering and Material Science, Duke University School of Engineering, and Niosôme + Perfected Age Treatment by L'ancôme of Paris; Page 1173, Lucas Meyer, Hamburg, Germany; Page 1177, Microfluidics Corp., Newton, Massachusetts; Pages 1180-1205, staff; Page 1206, Europa Crown; Page 1210, staff; Page 1219, International Food Information Council; Page 1227, Casey Croy.

"A Business and Scientific News
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1170 Calendar

1172 Feature

Manufacturers of personal care products and cosmetics are incorporating liposomes in their products as a means of providing more effective delivery and greater efficacy. INFORM senior editor/writer Barbara Fitch Haumann looks at whether liposomes are just a marketing gimmick or truly a way to offer functionality.

1180 World Conference

This section provides highlights from the World Conference and Exhibition on Oilseed Processing and Utilization, held Sept. 13-18, 1992, in Budapest, Hungary. This report includes a look at technical sessions, social events, poster sessions and the exhibition. Also presented are the two keynote addresses: "Transition Realities in Eastern Europe, the CIS" by Csaba Csaki and "The Search for Competitiveness" by David Swanson.

1211 Worldwatch

Included in this section is a report provided by Joseph R. Smith of Oilseeds International on the 13th International Sunflower Conference in Italy.

1214 Health & Nutrition

Anthony T. Diplock of the University of London summarizes findings on the role of antioxidant nutrients in disease.

1220 News

1223 From Washington

1226 Surfactants & Detergents

INFORM newswriter Casey Croy reports on the New Horizons '92 short course held in September.

1232 Processing

A. Rozenaal of the Oil Processing Division of Unilever describes the interesterification of oils and fats.

1239 Inside AOCS

1246 Methodology

1249 New Products

1253 Abstracts from AOCS journals

1261 Classified Advertising

Interesterification of oils and fats

Interesterification is one of three important fat modification processes. Unlike hydrogenation, it leaves the fatty acid composition unchanged and only alters the distribution of the fatty acids over the triacylglycerols. The stability of the oil remains essentially unchanged, but important physico-chemical properties such as melting, crystallization and recrystallization behavior are modified.

The precise effect of interesterification on the melting behavior depends very much on which type of starting material or mixture of starting materials is subjected to the interesterification process. If a fat of high melting point is interesterified with a liquid oil, there will be a (further) reduction of the melting point and of the solid fat content at various temperatures. The interesterification process will lead to an increased number of triacylglycerol types and therefore in most cases to a rather flat solid temperature curve. There is also a tendency that the wide range of triacylglycerol types present in interesterified fats results in a more regular crystallization process during the manufacturing of spreads and shortenings. Moreover, the rate of recrystallization processes during storage of such products may be retarded; β' -modification is stabilized and the transformation into the most stable β -modification proceeds more slowly.

Chemical background

Interesterification will lead to the so-called random distribution of fatty acids over the triacylglycerols if the process is carried out in a single phase with the usual types of catalysts. A random distribution means that the distribution of the fatty acids is determined only by chance, the resulting triacylglycerol is therefore predictable from the overall fatty acid composition of the mixture.

There are two exceptions to this random pattern. The first is directed interesterification (1). This process is carried out at such a low temperature that part of the triacylglycerols crystallizes. These solid triacylglycerols no longer participate in the reaction, which proceeds only in the liquid phase. The sec-



A. Rozenaal of the Oil Processing Division, Unilever Research Laboratory, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands, is the author of this article that originally appeared in *Edible Fats and Oils Processing: Basic Principles and Modern Practices*, the proceedings of an AOCS world conference. The proceedings was published by AOCS and is available from AOCS, PO Box 3489, Champaign, IL 61826-3489. The price is \$95 to AOCS members, \$125 to nonmembers, plus shipping costs.

ond exception occurs during interesterification with enzymes (2). Enzymes, such as lipases, can accomplish the exchange of fatty acids at the external positions of the triacylglycerol molecule but leave the fatty acid composition at the 2-position unchanged. The most obvious potential application of enzymatic interesterification is in the area of fats with triacylglycerol composition similar to that of cocoa butter,

i.e., with palmitic and stearic acid at the 1- and 3-positions and oleic acid at the 2-position.

In naturally occurring oils and fats, the fatty acids are not randomly distributed. In these oils, the so-called taxonomic patterns are well-established (Figure 1). For vegetable oils the fatty acid pattern usually conforms to the 1,3 random-2 random distribution pattern. The saturated fatty acids are almost

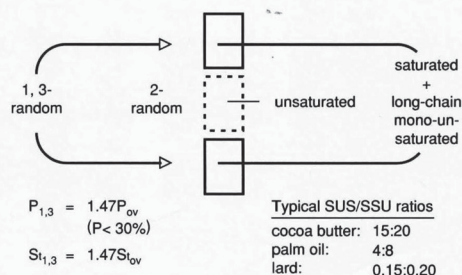


Figure 1. Taxonomic patterns of vegetable oils

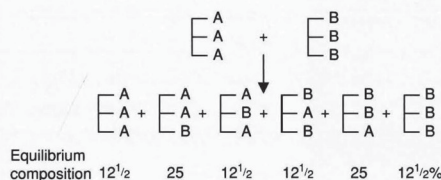


Figure 2. Interesterification of a binary mixture (50/50) of triacylglycerols

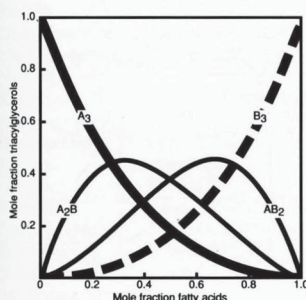


Figure 3. Randomized triacylglycerol composition in a binary mixture

exclusively concentrated at the 1,3-position and almost absent at the 2-position. The proportion of palmitic and stearic acid at the external positions is therefore approximately 1.5 x their overall proportion in the vegetable oil. These taxonomic patterns have a large influence on the ratio of symmetric to asymmetric triacylglycerols. The SUS/SSU (S = saturated; U = unsaturated) ratio in cocoa butter is about 15:20 and 4:8 in palm oil, whereas in an animal fat such as lard this ratio is far below 1.

In conclusion, natural fats have a nonrandom triacylglycerol composition, and the same is true for hydrogenated fats and fat fractions. Random distributions are obtained only by interesterification at temperatures above the melting point of the mixture.

If we interesterify two types of triacylglycerols, AAA and BBB, respectively, the redistribution of the fatty acids will result in an equilibrium mix-

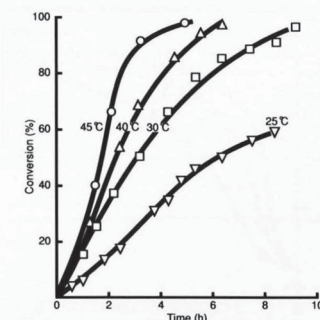


Figure 4. Interesterification of methyl myristate and butyl palmitate

ture of the six possible triacylglycerols (Figure 2). At equimolar amounts of A and B, the final reaction mixture will consist of 12.5% of each of the parent triacylglycerols AAA and BBB, and 37.5% of each of the intermediate triacylglycerols, of which 66% will be asymmetric and 33% will be symmetric.

This type of calculation can easily be extended to more complex situations. Figure 3 shows the random composition obtained in a mixture containing two fatty acids, A and B, in different molar fractions. The peak concentrations of the intermediate triacylglycerols A_2B and AB_2 occur at molar fractions of one-third and two-thirds, respectively. In Table 1 the number and amount of the various triacylglycerols obtainable by interesterification of a mixture containing different fatty acids are shown. For $n = 4$, 20 triacylglycerol types are obtained; for $n = 6$, 56 triacylglycerol types are formed.

Table 1
Theoretical triacylglycerol compositions after interesterification for n fatty acids (A,B,C,D, ...) with molar fractions a,b,c,d

Type	Number	Amounts
Mono-acid (AAA, BBB...)	n	a^3, b^3, c^3
Di-acid (AAB, AAC...)	$n(n-1)$	$3a^2b, 3ab^2, 3a^2c$
Tri-acid (ABC, BCD...)	$\frac{1}{6} n(n-1)(n-2)$	$6abc, 6acd...$
Total	$\frac{1}{6} n^3 - \frac{1}{2} n^2 + \frac{1}{6} n$	
	6 2 3	

Interesterification catalysts

Interesterification is a catalytic process involving the simultaneous breaking of existing ester bonds and the formation of new ones. In the absence of a catalyst, even extreme conditions of temperature and time will not give the desired result.

Numerous compounds have been proposed for speeding up the reaction at lower temperatures. Often the basic catalysts are used (Table 2) which include the alkali metals (sodium, potassium and their alloys) and the corresponding alcoholates (sodium methylate and ethylate). With these catalysts a fast interesterification reaction is possible at temperatures around 100°C. Sodium hydroxide is distinctly less active and requires reaction temperatures of at least 160°C. Sodium glycerate, which can be formed *in situ* from sodium hydroxide and glycerol (see below), is intermediate in activity.

Not active as interesterification catalysts are, for example, soaps (in fact, a well-known by-product formed during interesterification) and phenolates. These are inactive because of the strongly acidic nature of phenols, which makes the anion too stable to take part in interesterification reactions.

It is emphasized that the above catalysts should, in fact, be considered as pre-catalysts. The real interesterification catalyst is formed in the initial stages of the reaction and is the same for the various types of basic pre-catalysts.

Kinetics of interesterification

The kinetics of interesterification will be illustrated by three examples.

Table 2
Survey of interesterification catalysts

Type	Examples
Metals	Na, K, Na-K alloys
Alkoxides	CH_3ONa, C_2H_5ONa
Other types	$NaH, NaNH_2$ NaR (R = alkyl or phenyl)
Sodium hydroxide	
Sodium glycerate	from $NaOH + glycerol$

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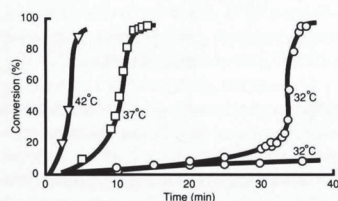


Figure 5. Interesterification of glycol esters of C_6 and C_8 acids (4)

First, there is interesterification of monoesters: methyl myristate and butyl palmitate [Figure 4 (3)]. The advantage of such a system is that the degree of conversion can be followed very easily by GLC (gas-liquid chromatography). Figure 4 shows that the degree of conversion goes up rapidly with increasing reaction temperature. Especially at the lower temperatures there is some evidence for the existence of an induction period.

The second example also refers to a model system, namely the short chain fatty acid esters (C_6 , C_8) of ethylene glycol [Figure 5 (4)]. In this case the induction period is very pronounced. The actual redistribution reaction appears to be very fast, even at temperatures as low as 30–40°C.

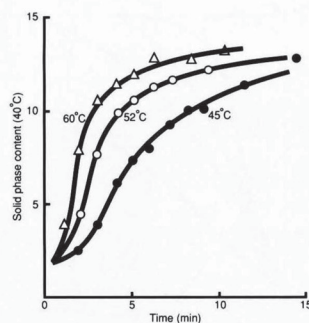


Figure 6. Interesterification of palm oil (4)

The third example refers to a practical oil (palm oil, Figure 6) (4). The solids content of 40°C was taken as a measure for the degree of interesterification. Again it can be seen that the reaction speeds up at higher temperatures and that at the lower temperatures there is evidence for an induction period.

These data strongly suggest that the added catalysts were indeed only precursors for the real interesterification catalyst, which is formed slowly during the initial stages of the reaction. This is confirmed by the fact that the induction period is completely absent when the catalyst is pre-dissolved in part of the oil or dosed as a molecular solution of, e.g., sodium methylate in methanol. The activa-

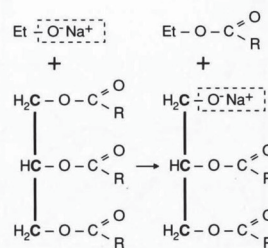


Figure 7. Activation of sodium ethylate

tion energy for the formation of the real interesterification catalyst apparently is higher than the activation energy for the interesterification reaction itself. During the reaction, the concentration of the real catalyst will not be constant: initially it will increase but later on it may decrease again, particularly at higher temperatures. For kinetic measurements it obviously is desirable to measure the real catalyst concentration. In our laboratory such a method, which is based on potentiometric titration of strong base in centrifuged oil samples, has been developed.

Mechanism of interesterification

The real interesterification catalyst is believed to be the sodium derivative of a diacylglycerol. Its formation from sodium ethylate and triacylglycerol is shown in Figure 7.

Ethyl esters are formed as a by-product but will be removed later during the deodorization process. For other pre-catalysts, similar schemes can be drawn up, e.g., in case of NaOH plus glycerol, during a first step sodium glycerate is formed, which subsequently reacts with triacylglycerol to form the real interesterification catalyst and monoacylglycerol as by-product (Figure 8).

The mechanism of the actual interesterification reaction (4,5) is shown in Figure 9. The slightly negative diacylglycerol anion attacks on the slightly positive carbon atom of the carbonyl group of one of the fatty acids of the triacylglycerol. The resulting transition complex will decompose to form

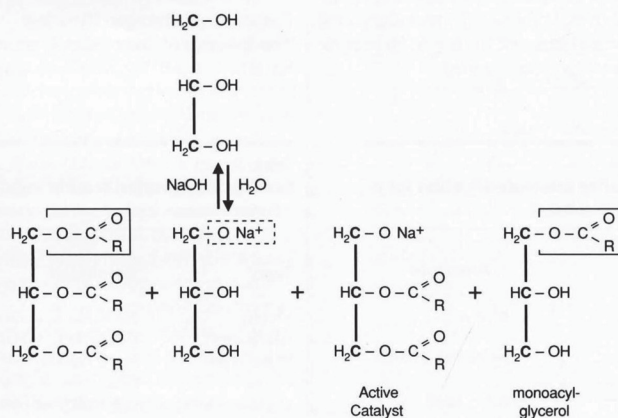


Figure 8. Formation of active catalyst from sodium hydroxide, glycerol and water

Table 3
Characteristics of batch sodium ethylate interesterification process

Stage	Condition
Pretreatment	FFA <0.1% soap <0.1% POV <10
Predrying	water <0.01%
Catalyst addition	100–110°C, 00.6 wt%
Reaction	100–110°C, 10–30 min
Cooling, washing, drying	

either the original triacylglycerol + active catalyst ion or form a new triacylglycerol + new active catalyst ion, which is then available for reaction with other triacylglycerol molecules, until eventually the reaction comes to an equilibrium.

Strong support for this mechanism has been provided by Steenhoek (4) who made a detailed investigation of the kinetics of interesterification of the glyceryl esters of saturated C₈ fatty acid and unsaturated C₁₀ fatty acid with pre-dissolved catalyst. The reaction was described by a set of six reactions between the various triacylglycerols and the various diacylglycerol anions (Figure 10). Each reaction was considered as an equilibrium reaction with, in principle, the same

Table 4
Properties of sodium alcoholates

	Property	Catalyst
	MeONa	EtONa
Bulk density (kg/l)	0.45–0.60	0.20–0.30
Average particle size (mm)	0.07	0.01–0.3
Shelf life (month)	3–6	2–3

reaction rate constant 3K. However, correction is necessary because not every possible exchange reaction leads to a net change in triacylglycerol composition. Therefore some of the reaction rate constants are effectively 2K and K.

Results of this simulation study are shown in Figure 11. Excellent agreement was obtained between the calculated (full) lines and the experimental data, not only for the triacylglycerol composition but also for the diacylglycerol anion composition. This is a very strong indication that the proposed interesterification mechanism is valid.

Process conditions

Industrial interesterification processes can be conducted in various ways: batchwise or continuously and with different types of catalyst. We confine ourselves mainly to two cases: (a) batch interesterification with

sodium methylate or ethylate as catalyst; and (b) continuous interesterification with sodium hydroxide and glycerol as catalyst.

The pretreatment requirements for the feedstock happen to be different as well for these two processes.

Batch interesterification

A summary of the feedstock requirements and the process conditions for interesterification with sodium methylate or ethylate is given in Table 3. Interesterification catalysts, being alkaline substances, are sensitive to acids, and it is therefore essential to carefully neutralize the feedstock to free fatty acid (FFA) levels below 0.1% before addition of catalyst. Higher FFA levels will necessitate the use of more catalyst: for each additional 0.05% FFA, about 0.01 wt% extra sodium ethylate is required.

Even more important is the role of water. Alcoholates such as sodium

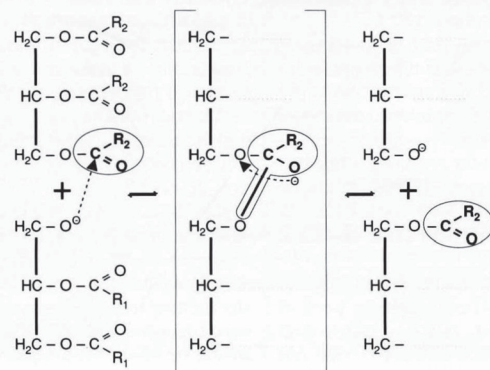


Figure 9. The mechanism of interesterification

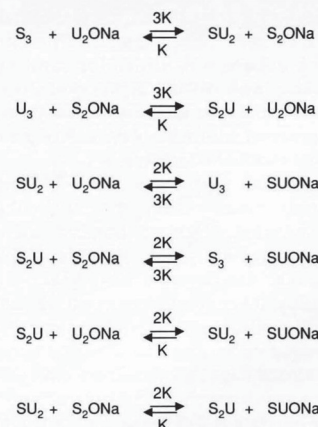


Figure 10. The kinetics of interesterification

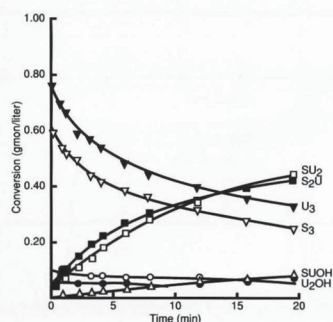


Figure 11. Computer simulation (solid points) vs actual experimental results (open points) of interesterification of a saturated ($S = C_{18}$) and an unsaturated ($U = C_{10:1}$) triacylglycerol (predissolved catalyst)

methyle and ethyle and also the real interesterification catalyst are very sensitive to inactivation by moisture. Oils to be interesterified should therefore be dried very thoroughly, preferably to below 0.01 wt% moisture. If more water is present, the required amount of catalyst will go up considerably: 0.01% water is equivalent to about 0.04% sodium ethyle.

Apart from free fatty acids and water, peroxides also have a negative effect on interesterification. Bleaching before interesterification therefore may be beneficial in that respect in addition to obtaining products of light color.

The interesterification reaction itself can be carried out at 100–110°C and generally will be completed within 30 min. No special equipment is required; conventional neutralizing-bleaching equipment with adequate facilities for catalyst dosing and oil-drying is suitable. Care should be taken to prevent any ingress of moisture, *i.e.*, valves and coils should be leakfree.

Sodium alcoholates are toxic and highly reactive materials and should be handled with care. Some of their properties are given in Table 4. To prevent deterioration of the catalyst quality, it is important to avoid contact with moisture and air and to store the catalyst under cool and dry conditions in closed bags and containers until the moment of use. The shelf life of sodium ethyle is 2–3 months, for sodium methyle, 3–6 months.

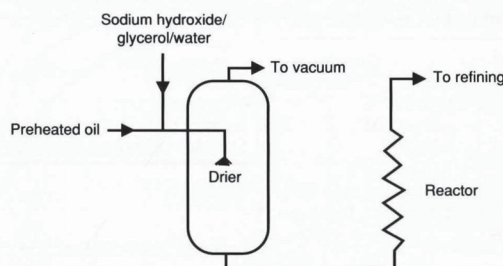


Figure 12. Principle of continuous sodium hydroxide/glycerol interesterification process

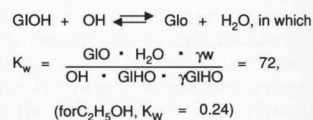
Continuous interesterification

In the past, various attempts have been made to develop interesterification processes based on sodium or potassium hydroxide, sometimes in combination with glycerol (6,7). Unilever owns patents (8) on a continuous interesterification process in which a solution of sodium hydroxide and glycerol in water is used as the pre-catalyst. A simple flow sheet is shown in Figure 12. Preheated oil is mixed with the catalyst solution, after which the mixture is spray-dried in a vacuum drier. In this unit also the real interesterification catalyst is formed. The interesterification reaction itself is a matter of minutes and can, for example, be carried out in a coil reactor with a narrow residence time distribution. The reaction temperature is about 130°C.

At first sight it may be astonishing that water is present in the catalyst solution, because, in general, moisture should be absent in interesterification reactions. However, in this case, the water is needed for obtaining a fine dispersion of catalyst particles in the oil; moreover, the water is flashed off immediately after the mixing of oil and catalyst solution.

A specific feature of this process is that the feedstock does not need to be neutralized. Neutralization and interesterification can be carried out in a single operation by increasing the amount of sodium hydroxide in the catalyst solution.

Glycerol in the catalyst solution has a beneficial effect because it reduces the rate of a competing reaction in which sodium hydroxide is converted into soap. This is due to the fact that the equilibrium between glycerol and hydroxyl ions lies at the righthand side of the equation:



and whereby the OH-concentration is reduced. Other consequences of this are that the glycerate anion is stabilized by internal resonance and that is less nucleophilic; so, it requires higher activation temperatures than ethyle, say 130°C against 100°C. After the activation stage, both catalysts are equivalent, because the same active catalyst is formed.

The final product control normally will be based on measurement of the solid phase content. For process control, however, there is no universally applicable method available. A method which is suitable for a certain product composition may fail in another situation. In most cases determination of the slip melting point or some standardized crystallization test can be used. Care should be taken that process conditions and feedstock quality are all right; in that case interesterification usually will take place to the desired degree.

Post-treatment and losses

All interesterification processes have in common the fact that ultimately the active catalyst is destroyed by addition of water, optionally with some acid to reduce oil losses by saponification in cases where the separation between oil phase and aqueous phase is delayed as may be the case in batch processing.

As a first approximation one may assume that all added catalyst is converted into soap. For the actual loss as soap, a refining or wash factor should also be taken into account which will, of course, be higher for batch refining than for centrifugal refining. Oil losses as soap can be calculated according to:

$$\frac{282}{40} \times \text{kgNaOH} \times \text{wash factor},$$

and

$$\frac{282}{68.5} \times \text{kg NAOEt} \times \text{wash factor}.$$

With alcoholate catalysts the loss as ethyl esters during the deodorization step is more or less equivalent to the amount of catalyst used in the interesterification process:

$$\frac{282}{68.5} \times \text{kg Na Et glycerol is recovered}$$

as diacylglycerol.

References

1. Eckey, E.W., *Ind. Eng. Chem.* 40:1183 (1948).
2. Macrae, A.R., *J. Am. Oil Chem. Soc.* 60:243 A (1983).
3. Jordan de Urries, M.P., and R.M. Utrilla, *Grasas y Aceites* 21:281 (1970).
4. Coenen, J.W.E., *Revue Franc. Corps Gras* 21:403 (1974).
5. Naudet, M., *Ibid.* 23:387 (1976).
6. Going, L.H., *J. Am. Oil Chem. Soc.* 44:414A (1967).
7. U.S. Patent 3.170.798 (1965).
8. U.S. Patent 4.585.593 (1986); EP 76.682 (1986). ■

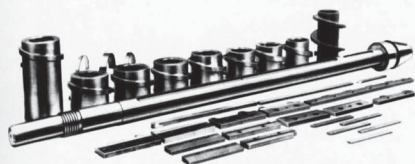
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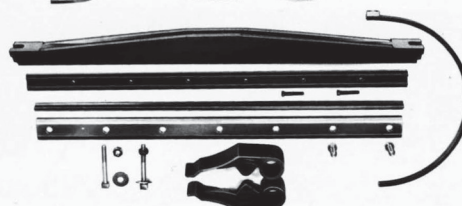
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