Methyl Esters in the Fatty Acid Industry

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ABSTRACT

Methyl esters, derived from natural fats or oils, can be used as alternatives to fatty acids in the production of a number of derivatives. The derivatives that can be made from methyl esters include fatty alkanolamides, fatty alcohols, isopropyl esters, and sucrose polyesters. By using methyl esters as the raw materials, several benefits may be realized, such as, the ability to make higher purity finished products, the use of milder conditions during syntheses, and the need for less expensive materials of construction. In addition to the applications mentioned, methyl esters are being used increasingly in fractional distillations because they have lower boiling points and are less corrosive than fatty acids.

INTRODUCTION

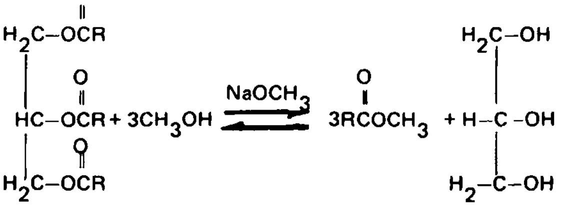
Fatty acids play an important role in the chemical industry because they are used as raw materials in the production of a number of very different derivatives. In this discussion, the prospects for using methyl esters as alternatives to fatty acids in the production of several of these derivatives are examined. Methyl esters can offer some unique benefits in these applications, as is shown later.

To explore this subject, this paper begins with a review of several of the industrial processes for preparing methyl esters. This is followed by a brief comparison of some of the properties of methyl esters and fatty acids that are relevant to fractional distillations. The final portion is devoted to examples of derivatives that can be made from either methyl esters or fatty acids.

There are several sources of information detailing the size of the fatty acid industry in the United States (1,2). Unfortunately, there is little documented information about the size of the methyl ester industry because the market for methyl esters is smaller, and a significant portion of these esters is used captively as intermediates in other syntheses. The few pieces of market data that are available pertain to specific derivatives or applications.

PRODUCTION OF METHYL ESTERS

Methyl esters are prepared in largest volume by the methanolysis of naturally occurring fats and oils with methanol in the presence of an alkaline catalyst, usually sodium methoxide (3–5).



$$\begin{array}{l} H_2C{-}O\overset{O}{\overset{\|}{C}}R \\ | \\ HC{-}O\overset{O}{\overset{\|}{C}}R \\ | \\ H_2C{-}O\overset{O}{\overset{\|}{C}}R \end{array} + 3CH_3OH \underset{}{\overset{NaOCH_3}{\rightleftharpoons}} 3R\overset{O}{\overset{\|}{C}}OCH_3 + \begin{array}{l} H_2C{-}OH \\ | \\ H{-}C{-}OH \\ | \\ H_2{-}C{-}OH \end{array}$$

(where R = alkyl group)

The driving force behind this equilibrium reaction is the separation of the methyl esters and glycerine into two phases. Excess methanol is used to improve the yields to acceptable levels.

As shown in the plant scheme in Figure 1, the methanol, catalyst, and refined oil are charged into an agitated vessel and allowed to react. This heterogeneous mixture is then pumped to a settling tank where the immiscible methyl ester phase and crude glycerine phase can separate. The crude glycerine solution is processed to recover high quality glycerol for sale and methanol for recycle; the ester stream is passed through a countercurrent water wash column to remove residual methanol, glycerine, and catalyst. After drying, the methyl esters are ready to be fractionated, reacted, or sold. This ester-making scheme can be used with any of the naturally occurring fats or oils; therefore, it does permit some flexibility in chain length selection.

Methyl esters have also been prepared by the direct esterification of fatty acids with methanol using an acid catalyst such as sulfuric acid (6,7). This process is generally used to make low grade methyl esters from low grade fatty acids or acidulated soapstocks, but with some modifications in the process and the feedstocks, high quality methyl esters could be manufactured. As will be shown later, some of the isopropyl esters used in cosmetics and plastics can be prepared in a similar fashion. Other routes for making methyl esters are available but are not presented here because they are not of commercial importance.

PROPERTIES OF METHYL ESTERS VS. FATTY ACIDS

If methyl esters instead of fatty acids are used as feedstocks for fractional distillations, three significant benefits are realized. The methyl esters are easier to fractionate, more stable, and less corrosive.

Generally, the esters are easier to fractionate because they have lower boiling points than the corresponding acids (8). As illustrated in Table I, the boiling points of the methyl esters average ca. 30 C lower than the acids, at 10 mm Hg pressure. This translates to a lower energy consumption and a lower risk of decomposition when fractionating methyl esters. These boiling point differences are due, in part, to the influence of hydrogen bonding. Methyl esters have a very limited capacity for hydrogen bonding because they contain no hydroxyl (–OH) groups; however, the

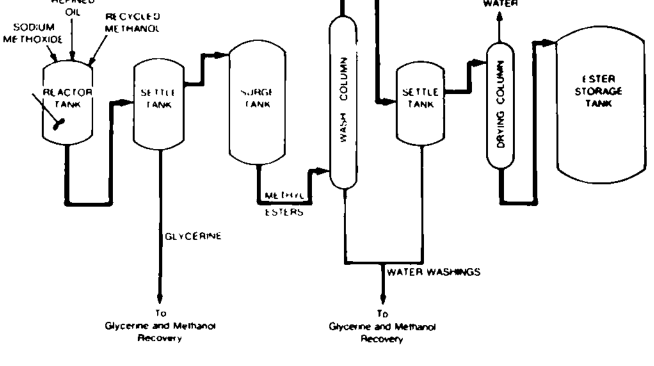
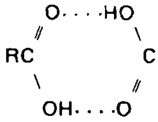


FIG. 1. Typical plant scheme for the interesterification of natural fats or oils with methanol.

fatty acids do have this functional group and are capable of hydrogen bonding.



(where . . . . indicates hydrogen bonding)

The extra energy needed to overcome these intermolecular attractions is reflected in the higher boiling points for the fatty acids. Because of the difference in intermolecular attractions, mixtures of methyl esters behave more ideally and obey Raoult's law better than mixtures of fatty acids do (9,10).

Another reason why methyl esters are preferred over fatty acids is associated with chemical stability. Fatty acids are susceptible to color formation and oxidative degradation (11 13), especially if they are heated; methyl esters do undergo these kinds of decompositions but not as readily. This difference is worth mentioning because stability is a major concern in most of the areas where methyl esters and fatty acids are used.

Methyl esters have another advantage because they are much less corrosive than fatty acids. Methyl esters can be processed in carbon steel equipment, but fatty acids need to be handled in more expensive stainless steel or other corrosion resistant equipment (14). This can lead to appreciable differences in equipment costs.

APPLICATIONS

It is appropriate to examine several of the applications where methyl esters and fatty acids compete with each other. The examples described here were chosen because they highlight more differences between using methyl esters vs. using fatty acids.

Alkanolamides

Perhaps the most notable application where methyl esters and fatty acids can be used to make similar derivatives is in the production of fatty alkanolamides. Alkanolamides have a multitude of uses, including detergents, foam boosters, thickening agents, emulsifying and wetting agents, plasticizers, antiblocking agents for plastics, and germicides (15–18). The largest quantities are used by the detergent and cosmetic industries because the alkanolamides function as essentially nonionic surfactants capable of stabilizing foam and building viscosity. The United States International Trade Commission (USITC) estimated that the 1977 production of alkanolamides in the U.S. totaled 81 million pounds (19). Of this amount, 37 million pounds was high active diethanolamides, 20 million pounds was low active diethanolamides, and the remaining 24 million pounds were monoethanolamine or other amine condensates. It is worthwhile to take a closer look at the alkanolamide area because its size is substantial.

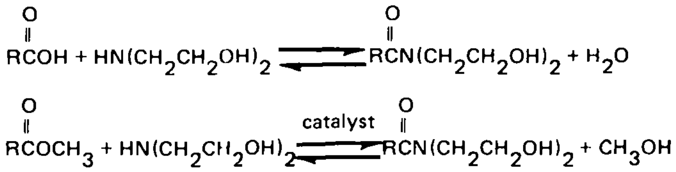
In 1937, Wolf Kritchevsky was issued the first patents (20,21) describing the preparation of alkanolamides from fatty acids or fatty acid derivatives using excess alkanolamines. Such alkanolamides are now commonly referred to as Kritchevsky or low active amides because they are typically 60–65% active. Edwin Meade taught an improved process in his 1949 patent (22) outlining the synthesis of alkanolamides from methyl esters using stoichiometric amounts of alkanolamines. These ester-derived alkanolamides are often called "super amides" as they are more than 90% active.

Consider the diethanolamides prepared by both routes (23–25).

TABLE I

Boiling Points of Methyl Esters and Fatty Acids at 10 mm Hg Pressure

Alkyl group	Boiling points (C)	
	Fatty acid	Methyl ester
Capric (C_{10})	150	108
Lauric (C_{12})	172	133
Myristic (C_{14})	192	161
Pentadecanoic (C_{15})	202	172
Palmitic (C_{16})	212	184
Margaric (C_{17})	220	195
Stearic (C_{18})	227	205
Arachidic (C_{20})	248	223
Behenic (C_{22})	263	240
Oleic (C_{18}=1)	223	201
Linoleic (C_{18}=2)	224	200
Linolenic (C_{18}=3)	224	202



$$\overset{O}{\overset{\parallel}{R C}}OH + HN(CH_2CH_2OH)_2 \rightleftharpoons \overset{O}{\overset{\parallel}{R C}}N(CH_2CH_2OH)_2 + H_2O$$

$$\overset{O}{\overset{\parallel}{R C}}OCH_3 + HN(CH_2CH_2OH)_2 \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} \overset{O}{\overset{\parallel}{R C}}N(CH_2CH_2OH)_2 + CH_3OH$$

While the two reactions appear to be similar, they are not. There are differences in the manufacturing processes and in the chemical compositions and physical characteristics of the end products.

Many of the manufacturing differences are highlighted in Table II. The reactant ratio plays an important part in determining the composition and behavior of the resulting alkanolamide. Also, because of its higher volatility, the methanol coproduct in the methyl ester reaction is easier to remove from the system than is the water coproduct in the fatty acid reaction. Therefore, lower reaction temperatures and shorter reaction times can be used when making alkanolamides from methyl esters. Finally, carbon steel can be used when esters are the starting compound; however, the reaction must be run in explosion proof equipment to accommodate the highly flammable methanol coproduct. Corrosion resistant materials are needed if fatty acids are used.

As mentioned, the chemical composition of an alkanolamide is highly dependent on the reactant ratio. This is illustrated in Table III. The lower diethanolamide content, higher amino-amine, diethanolamine, and amine soap contents in this Kritchevsky amide are direct results of the two-fold molar excess of amine required when fatty acids are used. Because there is no excess amine used in the methyl ester reaction, the byproduct content of the superamide is lower.

These chemical differences result in physical differences. Generally, the super amides are gels or solids at room temperature. These high active alkanolamides have low solubility in water but are readily solubilized in the presence of other surfactants. On the other hand, the low active alkanolamides are liquids when they are made from coconut fatty acids or lauric acids. Furthermore, they are soluble in water because they contain a considerable amount of free amine and amine soap.

The physical and chemical differences between the two types of alkanolamides naturally lead to differences in their end uses. The super amides are preferred for shampoos and light duty liquids where their high purity makes them more efficient than the low active alkanolamides in stabilizing foam and building viscosity. Super amides are also desired for other applications where high purity or aesthetics is important. The low active amides are particularly suitable

TABLE II

Alkanolamide Reaction Comparison

Characteristic	Starting material $R\overset{O}{\overset{\Vert}{C}}OH$	 $R\overset{O}{\overset{\Vert}{C}}OCH_3$
Reactant ratio (molar)	2:1 (amine:acid)	1:1 (amine:ester)
Catalyst	None	$NaOCH_3$
Co-product	Water	Methanol
Temperature	140–160 C	90–115 C
Time	6 hr	4 hr
Pressure	Atmospheric	Reduced
Material of construction	Stainless steel	Carbon steel/explosion proof

TABLE III

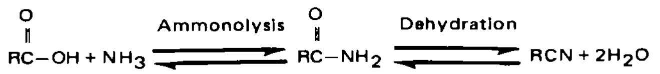
Typical Composition of Diethanolamides

Component	Composition Low active or 2:1 amide (from fatty acid)	 Super amide or 1:1 amide (from methyl ester)
Diethanolamide[a]	55%	90%
Amido-amine[a]	10%	Trace
Free diethanolamine	22%	5%
Amine soap	10%	Trace
Amide ester	1%	4%
Water	2%	Trace
Methanol	---	0.2%
Methyl ester	---	0.8%

[a] The Amido-amine portion is usually reported in the diethanolamide content.

for hard surface cleaners where their good solubility and detergency are valuable. These kinds of applications do not demand high purity components.

Alkanolamides and simple amides (26) are also used as intermediates in the production of other chemicals. Nitriles, for example, have been manufactured in a continuous process by first reacting a fatty acid with ammonia. The resulting amide is then dehydrated to give the nitrile (27,28).



$$R\overset{O}{\overset{\Vert}{C}}-OH + NH_3 \underset{}{\overset{\text{Ammonolysis}}{\rightleftharpoons}} R\overset{O}{\overset{\Vert}{C}}-NH_2 \overset{\text{Dehydration}}{\rightleftharpoons} RCN + 2H_2O$$

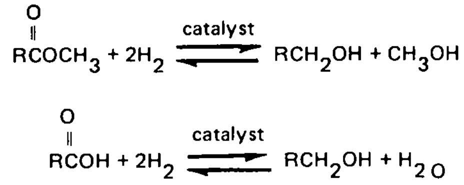
Nitriles could be prepared from the methyl esters, although this is not generally done. These nitriles are used chiefly to make tertiary amines and amine derivatives, such as quaternary amines and amine oxides.

Other products that can be made from the amides include sulfated (29,30) and ethoxylated (31) alkanolamides. Betaines (32,33) and imidazolines (27,34), the so-called low irritation shampoo surfactants (35) that are becoming increasingly important, can also be prepared from alkanolamide intermediates.

The decision to start with the methyl ester or the fatty acid will again depend on processing needs and end-use requirements. In the case of the diethanolamides, the ester-derived products and acid-derived products are very different. In the next example, the products are essentially equivalent, regardless of the starting material.

Fatty Alcohols

Fatty alcohols (36–38) are a second group of compounds that can be prepared from either methyl esters or fatty acids.



$$R\overset{O}{\overset{\Vert}{C}}OCH_3 + 2H_2 \overset{\text{catalyst}}{\rightleftharpoons} RCH_2OH + CH_3OH$$

$$R\overset{O}{\overset{\Vert}{C}}OH + 2H_2 \overset{\text{catalyst}}{\rightleftharpoons} RCH_2OH + H_2O$$

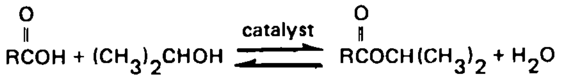
Conversions in excess of 90% can be achieved with hydrogen pressures of 200 -300 atmospheres (3000–4500 psi) and temperatures of 290–330 C. The hydrogenolysis of the methyl esters is the preferred route because reaction conditions toward the lower ends of these ranges can be used. Additionally, equipment costs are lower for the methyl ester system because corrosion resistant materials are not needed.

Fatty alcohols are found in a variety of products. For instance, the C_6–C_{11} alcohols, commonly termed plasticizer alcohols, are used in plastics, lubricants, and agricultural chemicals. The C_{12}–C_{14} detergent range alcohols are used to make surfactants, emulsifiers, lubricant additives, and antioxidants. Finally, the C_{16} and C_{18} alcohols and their derivatives are used chiefly in cosmetic or pharmaceutical products.

Isopropyl Esters

A third family of products that can be made from either methyl esters or fatty acids consists of the isopropyl esters which are used as plasticizers or emollients. As an example, isopropyl myristate can be prepared by either the alcoholysis of methyl myristate (39,40) or the esterification of myristic acid (6,7).

$$\mathrm{R\overset{\overset{O}{\|}}{C}OCH_3 + (CH_3)_2CHOH \xrightleftharpoons{catalyst} R\overset{\overset{O}{\|}}{C}OCH(CH_3)_2 + CH_3OH}$$



$$\mathrm{R\overset{\overset{O}{\|}}{C}OH + (CH_3)_2CHOH \xrightleftharpoons{catalyst} R\overset{\overset{O}{\|}}{C}OCH(CH_3)_2 + H_2O}$$

These two reactions were chosen because they point out another difference between methyl esters and fatty acids. An azeotrope forms between the isopropyl alcohol and the water produced in the fatty acid reaction. This makes it somewhat difficult to recover the excess isopropyl alcohol for recycle. Isopropyl alcohol does not form an azeotrope with the methyl alcohol that is produced in the methyl ester reaction; hence, the separation of these two alcohols is easier.

The USITC estimated the 1977 production of isopropyl myristate was 3.1 million pounds. No estimates for isopropyl palmitate or isopropyl oleate were given although they were produced in that year.

New Developments

The methyl ester and fatty acid derivatives that have been reviewed so far have been known for some time. There are, however, experimental products that are currently being synthesized from these chemicals. Sucrose polyesters (SPE) are a good example. These highly substituted sucrose esters (6–8 alkyl groups per molecule of sucrose) have received considerable attention recently (41,42) because they have been found to be noncaloric substitutes for dietary fats in tests conducted by the Procter & Gamble Company (43). Furthermore, SPE appear to be useful agents for reducing plasma cholesterol (44). To meet the standards necessary for this potential food application, the Procter & Gamble development group made these sucrose polyesters from methyl esters (45) instead of from fatty acids or soaps. Undoubtedly, there are other examples of new products that can be made from methyl esters more easily than from fatty acids.

The decision to use methyl esters instead of fatty acids is not always an easy one to make. Each application has its own set of concerns that must be addressed. Some of the questions that need to be asked before making this decision are: (a) what product quality constraints must be met? (b) can the quality requirements be satisfied using methyl esters as the raw material? . . . using fatty acids as the raw materials? (c) what equipment, new or existing, is needed? (d) assuming that it is technically feasible to make the product, is it economically feasible to sell?

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