

1

Fatty Acids and Derivatives from Coconut Oil

Gregorio C. Gervajio

1. THE WORLD'S FATS AND OILS OUTPUT

The oleochemical industry is fairly well developed and its future secure because of a reliable supply of raw materials. The world's fats and oils output has been growing rapidly over the past few decades, far beyond the need for human nutrition. The world's production and consumption of natural oils and fats has grown from 79.2 million t in 1990 to 117 million t in 2001. Malaysia, Indonesia, and Argentina are notable excess-supply producers; India, the European Union countries, and China are notable high-demand areas that supplement regional production through imports (1).

The principal raw materials from which the natural fatty acids are derived are tallow, crude tall oil, coconut, palm kernel, and soybean oils.

Many new fatty acid plants have been built in Southeast Asia, which is a major source of coconut and palm oils used as raw materials for the production of C8–C14 fatty acids. Altogether, those countries (excluding China and India) have producers of fatty acids from oil splitting with a capacity of 1.5 million t. Significant amounts of the increasing production are being exported to other areas, including the United States, Western Europe, and Japan (2).

The Philippines, a major producer of coconut oil, established its first oleochemical plant of limited capacity in 1967. The plant produced only 3,000 t/year of coco

fatty alcohols using KAO's technology via the methyl ester route. This was followed by a moderate-size plant, a joint venture between KAO Japan and a local partner commissioned in 1980, producing 25,000 t of coco fatty alcohol and a host of oleochemical derivatives.

COCOHEM's cocochemical plant, established in 1984, was the biggest in the region during that period, with a splitting capacity of 70,000 t crude coconut oil and producing 36,000 t of fatty alcohols, 9,000 t of glycerine, and various cuts of fatty acids and fatty alcohols. The plant uses the Lurgi technology of the hydrogenation of fatty acids to produce fatty alcohols. Recent data for the Phillippines listed a capacity of 25,000 t of alcohol products from coconut oil by the fatty acid hydrogenation process for Coccochem and 4,000 t for Colgate. Phillippinas Kao produced 30,000 t of alcohol products from coconut oil using the methyl ester hydrogenation process (3). Consumption of fatty acids in the United States, Western Europe, and Japan totaled 2.5 million t in 2001. There was a sharp decline in production and consumption of fatty acid in North America after the events of September 2001. However, growth is expected at the rate of 2.3% for the consumption of split acids for the period 2000–2006. Growth in Western Europe is expected at the rate of 1.2%/yr for the period 2001–2006. Japan's consumption is expected to decline (2).

2. THE ROLE OF COCONUT OIL IN THE OLEOCHEMICAL INDUSTRY WORLDWIDE

Coconut oil and palm kernel oil, a coproduct of palm oil, comprise less than 5% of the total natural fats and oils, but they are important feedstocks of the oleochemical industry.

Coconut oil is commercially a major source of lauric acid. Together with palm kernel oil and, to a small extent, babassu oil, it belongs to the so-called lauric oils, which are characterized by their high lauric oil content of approximately 50%.

The lauric oils are highly desirable materials in the oleochemical industry worldwide because of the importance of the lauric fraction especially in the manufacture of soaps and detergents (4).

Coconut oil is well positioned because it has the unique advantage of having its fatty acid composition falling within the carbon chain spectrum highly desired by the oleochemical industry where the C12 and C14 fatty acid fractions are sought after. Table 1 shows the fatty acid composition of coconut oil and palm kernel oil.

The caproic to capric (C6–C10) fatty acid fractions comprising approximately 15% are good materials for plasticizer range alcohol and for polyol esters. The latter are used in high-performance oil for jet engines and for the new generation of lubricants. These acid fractions are also the basic material for the manufacture of medium-chain triglycerides, a highly valued dietary fat.

The C12–C18 fatty acid fractions, approximately 85% of the coconut oil fatty acid composition, are the primary raw materials for detergent-grade fatty alcohols. Coconut oil is a primary source of basic oleochemicals and a host of other oleochemical derivatives. Figure 1 indicates some of the major processes by which

TABLE 1. Fatty Acid Composition of Coconut and Palm Kernel Oils (5).

Fatty Acid	Formula	Coconut Oil (%)	Palm Kernel Oil (%)
Caproic	$C_6H_{12}O_2$	0.2–0.8	0–1
Caprylic	$C_8H_{16}O_2$	6–9	3–5
Capric	$C_{10}H_{20}O_2$	6–10	3–5
Lauric	$C_{12}H_{24}O_2$	46–50	44–51
Myristic	$C_{14}H_{28}O_2$	17–19	15–17
Palmitic	$C_{16}H_{32}O_2$	8–10	7–10
Stearic	$C_{18}H_{36}O_2$	2–3	2–3
Oleic	$C_{18}H_{34}O_2$	5–7	12–19
Linoleic	$C_{18}H_{32}O_2$	1–2.5	1–2

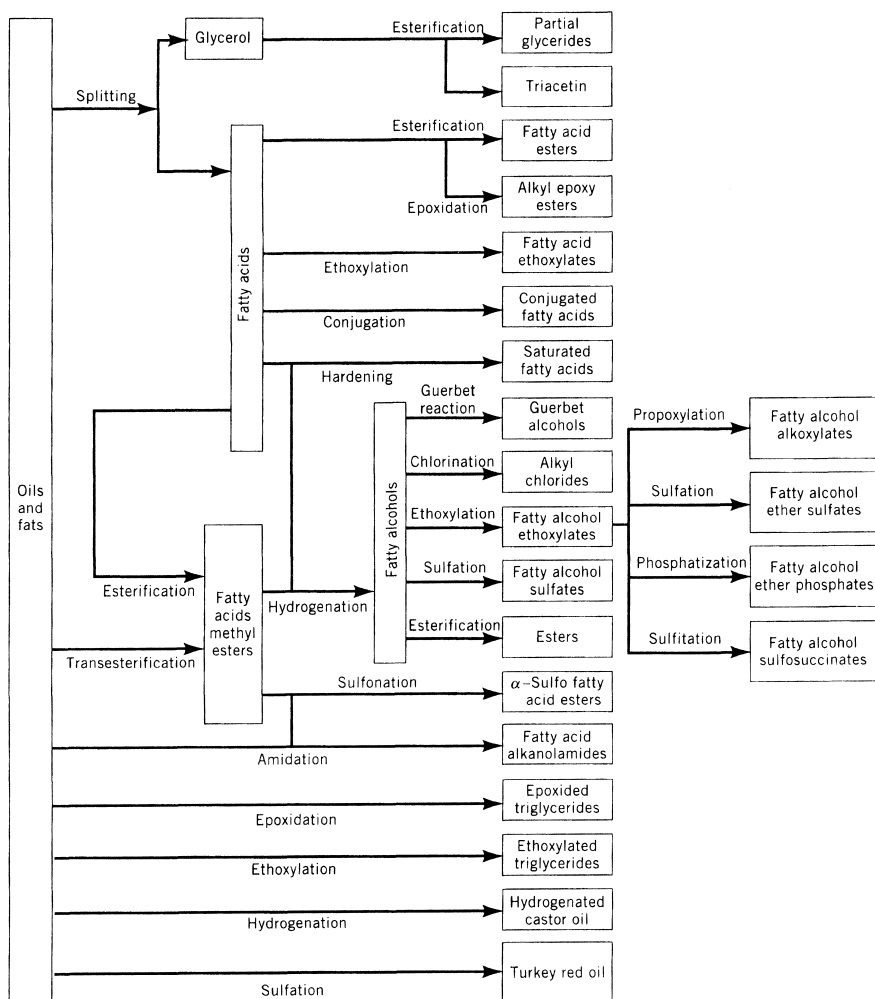


Figure 1. Oleochemical raw materials and their derivatives (6).

various oleochemicals and their derivatives can be obtained from fats and oils. These processes are applicable to coconut oil with the exception of epoxidation and direct sulfation because coconut oil lacks the necessary unsaturation to initiate the two reactions. As can be seen from Figure 1, a great number of oleochemicals can be derived from natural fats and oils. These oleochemicals find increasing use in various applications.

3. TYPES OF FATTY ACIDS AND DERIVATIVES FROM COCONUT OIL AND THEIR GENERAL APPLICATIONS

Coconut oil is one of the most important raw materials for the oleochemical industry. The whole range of its fatty acid composition is used as the starting material for a wide variety of oleochemical products. Fatty acids are the building blocks that, with proper selection and application of oleochemistry, are converted to higher valued products.

Coconut oil is considered a saturated oil. From Table 1, it can be seen that coconut oil has approximately 92% saturated fatty acid, from caproic to stearic, and only around 8% unsaturated fatty acid, composed of oleic acid and linoleic acid.

3.1. Types of Fatty Acids from Coconut Oil

Fatty acids obtained by the high-pressure splitting of coconut oil, as discussed later in this Chapter, are distilled and can be fractionated into various fractions or individual cuts. Types commercially available are the following (7).

1. *Whole distilled coconut fatty acid.* A refined product whose fatty acid composition is identical to that of the original oil.
2. *Caprylic, capric acid.* The low-molecular-weight fraction comprising around 55% C8 and 40% C10 fatty acid fractions with small amounts of C6 and C12 fractions.
3. *Topped coconut fatty acid.* The C12–C18 fraction after topping off the C8–C10 fraction.
4. *Lauric, myristic acid.* The medium-chain fatty acid fraction comprising approximately 72% C12 and 26% C14 fatty acid fractions with traces of C10 and C16 fatty acid fractions.
5. *Lauric acid.* A pure-cut C12 fatty acid with a purity of 99% minimum with traces of C10 and C14 fatty acid fractions.
6. *Myristic acid.* A pure-cut C14 fatty acid with a purity of 98% minimum and traces of C12 and C16 fatty acid fractions.

There is a market for individual cuts of fatty acids of high purity. These are highly desired by certain industries, such as the cosmetic industry, and command higher prices.

Table 2 shows the typical composition and properties of these types of fatty acids as produced by United Coconut Chemicals Philippines, Inc.

TABLE 2. Fatty Acid Product Specifications (7).

Fatty Acid Products	Product Code	Iodine Value	Acid Value	Saponification Value	Titer (°C)	Unsapnifiable Matter		Approximate Carbon Chain Distribution									
						(% maximum)	(maximum)	Y	R	C6	C8	C10	C12	C14	C16	C18	C18:1
Whole distilled coconut fatty acid (C8-C18)	Philacid 0818	6-10	268-274	269-275	21-25	0.5	15	1.5	0.5	7.5	6.5	48	18	9	2	7	2
Caprylic-capric acid (C8-C10)	Philacid 0810	0.8 maximum	355-365	356-366	1-5	0.5	—	—	4	55	39	3	—	—	—	—	—
Topped coconut fatty acid (C12-C18)	Philacid 1218	8-12	254-260	254-260	25-29	0.5	15	1.5	—	—	1.0	55	22	10	2.5	8	2
Lauric acid (C12)	Philacid 1200	0.3 maximum	279-281	279-281	42-43	0.5	8	0.8	—	—	0-1	99 min.	0-1	—	—	—	—
Myristic acid (C14)	Philacid 1400	0.3 maximum	245-247	245-247	53-54	0.5	8	0.8	—	—	—	0-2	98 min.	0-2	—	—	—
Lauric-myristic acid (C12-C14)	Philacid 1214	0.5 maximum	268-273	268-273	33-35	0.5	10	1.0	—	—	1	72	26	1	—	—	—

3.2. Oleochemical Derivatives from Coconut Oil and Their General Applications

Coconut fatty acids and their various fractions, aside from being used directly, are converted further to other derivatives. Their range of application covers a broad spectrum in the oleochemical industry. As shown in Figure 1, fatty acids can undergo different processes in the manufacture of various oleochemical derivatives. Among the more common products and applications are the following:

Fatty Acids. A large volume of coconut fatty acids are used as major components in toilet soap manufacture. Its high lauric content provides the quick lathering properties of toilet soap.

Fatty Acid Esters. Different fatty acid fractions can be esterified with a monoalcohol or a polyol to yield various esters. Polyol esters of trimethylol propane or pentaerythritol and C8–C10 fatty acids are the bases for high-performance lubricants. Re-esterification of C8–C10 fatty acid with glycerol yields a medium-chain triglyceride, a low-viscosity, highly stable oil. Medium-chain triglyceride is used as a solvent for flavors, in the surface treatment of dried fruits, and as a high-energy, readily digestible dietary fat.

Esterification with monoalcohol, such as isopropanol and myristic acid, yields isopropyl myristate, an important cosmetic ingredient. Glyceryl monoesters and wax esters find application as food emulsifiers, mold release agents, and lubricants for the plastic industry.

Fatty Alcohols. Fatty alcohol is considered a basic oleochemical manufactured by high-pressure hydrogenation of fatty acids or fatty acid methyl esters. The majority of the fatty alcohol produced is further subjected to various processes, such as sulfation, ethoxylation, amination, phosphatization, sulfitation, and others.

Fatty alcohol can be fractionated to separate the C8–C10 fraction, known as plasticizer range alcohol, and the C12–C18, known as the detergent range alcohol. The plasticizer range alcohol is a liquid with good dissolving power. It can be used in a limited way as a solvent for printing inks and lacquers. Esterification with a polycarboxylic acid, such as phthalic anhydride, yields an excellent plasticizer especially for PVC.

The C12–C14 alcohol finds special application as lubricant additives and in the formulation of bearing and hydraulic oils. The C16–C18 fatty alcohol finds application as a defoamer, as a solubility retarder for syndet bars, and as a consistency giving factor in creams, lipstick, pastes, and polishes.

By far, the greatest application of fatty alcohol is in the manufacture of fatty alcohol sulfate and fatty alcohol ether sulfate. These materials possess good foaming properties and ready biodegradability and are extensively used as base surfactants for laundry detergent products, shampoos, dishwashing liquids, and cleaners.

Polyglycol Ethers. Polyglycol ethers, produced by the reaction of fatty alcohol with ethylene oxide, constitute the most important class of nonionic surfactants. They possess good wetting properties, produce relatively low foam, and are highly effective at low temperature and low concentration. They are used as textile auxiliaries, in dishwashing liquids, degreasing products, and liquid cleaner formulations.

Other Specialty Surfactants. Monoalkyl phosphate, fatty alcohol ether phosphate, and fatty alcohol sulfosuccinate are some of the specialty surfactants derived from fatty alcohol with specific applications in the cosmetics and other chemical industries.

Fatty Amides. Cocomonethanolamide and cocodiethanolamide formed by the reaction of fatty acids or esters with monoethanolamine or diethanolamine are popularly used as foam boosters for shampoos and detergent products.

Fatty Amines. Fatty amines are the most important nitrogen derivatives of fatty acids. They are produced by the reaction of fatty acids with ammonia and hydrogen. They are the bases for the manufacture of quaternary ammonium compounds used as fabric softeners and biocides. Fatty amine oxides are mild to the skin with good cleaning and foaming properties and find application as a shampoo ingredient. The above mentioned products are but some of the oleochemical derivatives from coconut fatty acids (5).

3.3. Principles and Methods in the Manufacture of Oleochemicals

Oleochemicals, by their very name, may be defined as chemicals from oil. These could be natural fats and oils, or oils of petrochemical origin. To have a clear distinction, oleochemicals derived from natural oils are termed natural oleochemicals, whereas those derived from petrochemicals are termed synthetic oleochemicals (8).

The natural oleochemicals are obtained from natural oils with the least change in the structure of the carbon chain fraction. In contrast, synthetic oleochemicals are built up from ethylene to the desired carbon chain fraction or from oxidation of petroleum waxes.

Fats and oils are renewable products of nature. One can aptly call them “oil from the sun” where the sun’s energy is biochemically converted to valuable oleochemicals via oleochemistry. Natural oleochemicals derived from natural fats and oils by splitting or *trans*-esterification, such as fatty acids, methyl esters, and glycerine are termed basic oleochemicals. Fatty alcohols and fatty amines may also be counted as basic oleochemicals, because of their importance in the manufacture of derivatives (8). Further processing of the basic oleochemicals by different routes, such as esterification, ethoxylation, sulfation, and amidation (Figure 1), produces other oleochemical products, which are termed oleochemical derivatives.

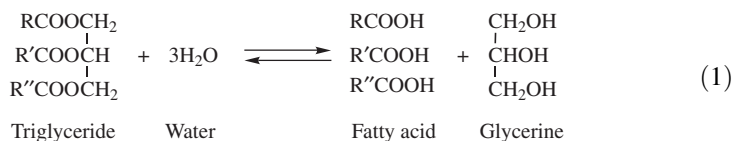
The succeeding discussions detail the processing methods in the manufacture of the basic oleochemicals and their derivatives.

4. FATTY ACIDS

Fatty acids and fatty acid methyl esters are probably the most important basic oleochemicals in the oleochemical industry. Fatty acids are used as starting materials for soaps, medium-chain triglycerides, polyol esters, alkanolamides, and many more.

4.1. Chemistry of Fat Splitting

Coconut oil, like any other fat or oil, can be hydrolyzed or split into its corresponding fatty acids and glycerine. The reaction is represented by the following equation:



In the case of coconut oil, the fatty acid fractions are C8 to C18 with a trace amount of C6.

Fat splitting is essentially a homogeneous reaction that proceeds in stages. The fatty acid radicals are displaced from the triglyceride one at a time from tri to di to mono. An incomplete splitting will thus contain monoglycerides and diglycerides as well as triglycerides. During the initial stage, the reaction proceeds slowly, limited by the low solubility of the water in the oil phase. In the second stage, the reaction proceeds fairly rapidly brought about by the greater solubility of water in the fatty acids. The final stage is characterized by a diminishing reaction rate as the fatty acids liberated and the glycerine byproduct reach equilibrium conditions.

Fat splitting is a reversible reaction. At the point of equilibrium, the rates of hydrolysis and re-esterification are equal. The glycerine byproduct must be withdrawn continuously to force the reaction to completion.

Increasing the temperature and pressure accelerates the reaction because of the increased solubility of the water in the oil phase and to its higher activation energy. Temperature, in particular, exerts a significant effect. An increase in temperature from 150°C to 220°C increases water solubility by two to three times.

The presence of small amounts of mineral acids, such as sulfuric acid or certain metal oxides, such as zinc or magnesium oxide, accelerates the splitting reaction. These metal oxides are true catalysts. They also assist in the formation of emulsions.

4.2. Fat-Splitting Processes

There are at least four known methods of fat splitting. These are (1) Twitchell process, (2) batch autoclave process, (3) continuous process, and (4) enzymatic process.

Twitchell Process. The Twitchell Process (9) is one of the earliest processes developed for fat splitting. It is still used in a small way because of its low initial cost and simplicity of installation and operation. However, it is no longer of great commercial importance, due to its high-energy consumption and poor product quality. The process makes use of the Twitchell reagent and sulfuric acid to catalyze the hydrolysis. The reagent is a sulfonated mixture of oleic or other fatty acid and naphthalene.

The operation is carried out in a wooden, lead-lined, or acid-resistant vat where the fat, water amounting to approximately half the fat, 1–2% sulfuric acid, and 0.75–1.25% Twitchell reagent are boiled at atmospheric pressure for 36–48 h, using open steam. The process is usually repeated two to four times, drawing off the glycerine–water solution after each stage. At the last stage, water is added and the mixture boiled to wash off any remaining acid.

The long reaction period, high-steam consumption, and discoloration of the fatty acids are disadvantages of the process and are the reasons for its limited use today.

Batch Autoclave Process. The batch autoclave process is the oldest commercial method used for splitting higher grade stock to produce light-colored fatty acids. It is also more rapid than the Twitchell process, taking about 6–10 h to complete. Distillation is normally performed to remove glyceride esters.

This process uses a catalyst, usually zinc, magnesium, or calcium oxides. Of these, zinc is the most active. About 2–4% catalyst is used, and a small amount of zinc dust is added to improve the color of the fatty acids.

The autoclaves are tall cylinders, 1220–1829 mm in diameter and 6–12 m high (10) made of corrosion-resistant alloy and fully insulated. An injection of live steam provides the agitation, although some, in addition, use mechanical agitators.

In operation, the autoclave is charged with the fat, water amounting to about half the fat, and the catalyst. Steam is blown through to displace any dissolved air, and the autoclave is closed. Steam is admitted to raise the pressure to 1135 kPa and is injected continuously at the bottom while venting a small amount to maintain the desired agitation and operating pressure. More than 95% conversion is achieved after 6–10 h. The contents of the autoclave are transferred to a settling tank where two layers are formed: the fatty acid upper layer and the glycerine (sweetwater) lower layer. The fatty acid layer is drawn off, treated with mineral acid to split the soap formed, and finally washed to remove traces of the mineral acid.

Continuous Process. The continuous countercurrent, high-pressure fat-splitting process, more popularly known as the Colgate–Emery process, is the most efficient of the current methods of fat hydrolysis. The high temperature and pressure used permit short reaction time. Full countercurrent flow of oil and water produces a high degree of splitting without the need of a catalyst. However, a catalyst may be used to increase reaction rate further.

The splitting tower is the heart of the process. Most splitting towers have the same configuration and basically operate the same way. Depending on the capacity, the tower can be 508–1220 mm in diameter and 18–25 m high and is made of corrosion-resistant material such as stainless steel 316 or Inconel alloy designed to operate at a pressure of about 5000 kPa.

Figure 2 shows a Lurgi single-stage countercurrent splitting plant. The deaerated fat is introduced by means of a sparge ring, around 1 m from the bottom with a high-pressure pump. Water is introduced near the top at a ratio of 40–50% of the weight of the fat. The high splitting temperature (250–260°C) ensures adequate dissolution of the water phase into the fat so that mechanical means for bringing the two phases into contact are not required.

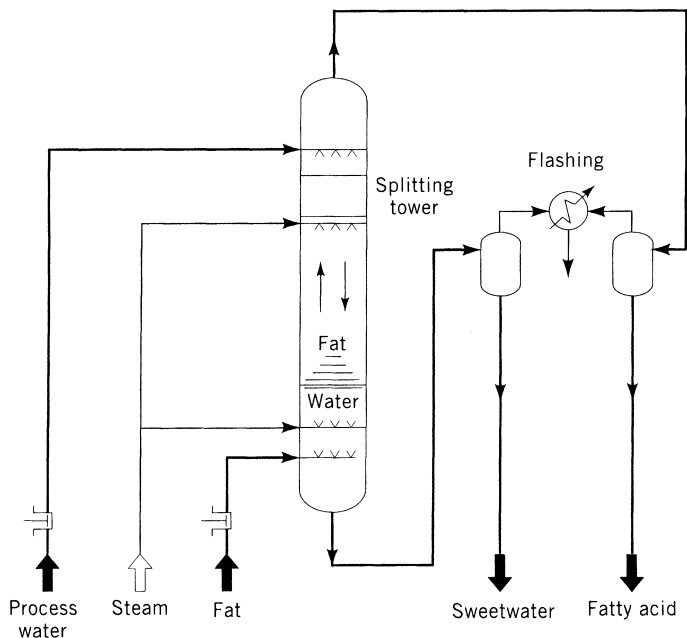


Figure 2. Single-stage countercurrent splitting (11).

The empty volume of the tower is used as the reaction compartment. The crude fat passes as a coherent phase from the bottom to the top through the tower, whereas the heavier splitting water travels downward as a dispersed phase through the mixture of fat and fatty acid. Degrees of splitting up to 99% can be reached (11).

The continuous countercurrent high-pressure process splits fats and oils more efficiently than other processes in a reaction time of only 2–3 h. Little discoloration of the fatty acids occur. As a result of the efficient internal heat exchange, this process affords high steam economy.

The utilities consumption per ton of feed is as follows (11).

Steam (6000 kPa)	190 kg
Cooling water (20°C)	3 m ³
Electrical energy	10 kWh
Process water	0.6 m ³

Enzymatic Splitting. Fats and oils can hydrolyze in the presence of natural enzymes. Fat splitting through the use of lipolytic enzymes had been carried out in experimental trials. However, at present, this process is of doubtful importance because of its high cost and long reaction time.

The enzymatic splitting of fats and oils by lipase from *Candida Rugosa*, *Aspergillus niger*, and *Rhizopus arrhizus* had been studied at a temperature range of 26–46°C for a period of 48–72 h. About 98% splitting is possible (12). There are

still major problems to be solved in the further development of this process before it becomes commercially viable.

4.3. Fatty Acid Distillation and Fractionation Operations

The fatty acids produced from the various fat-splitting processes are purified and separated into fractions or even individual fatty acids by distillation and fractionation.

Fatty Acid Distillation. Distillation of crude fatty acids removes both the low and high boiling impurities as well as odor bodies. Fatty acids are extremely sensitive to heat, oxidation, and corrosion effects. This is due to the reactive acid group at the end of the long carbon chain. These factors are taken into consideration in the design of the distillation unit and its operating parameters. Distillation is carried out under high vacuum and lower temperatures and with the shortest residence time allowable.

Technical design of most distillation units features high vacuum with no allowance for air leakage, effective heating to achieve short contact time, good circulation for effective mass transfer between vapor and condensate, and steam economy. Internal arrangements of the column vary among suppliers with the ultimate purpose of achieving the design objectives. The basic steps in processing are about the same. Figures 3 and 4 show Badger's and Lurgi's continuous fatty acid distillation plants.

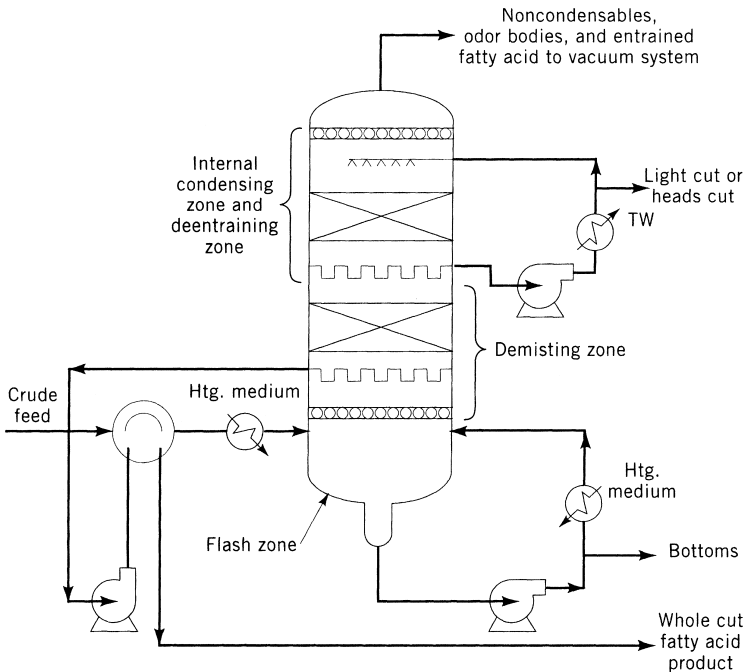


Figure 3. Badger's continuous fatty acid distillation (13).

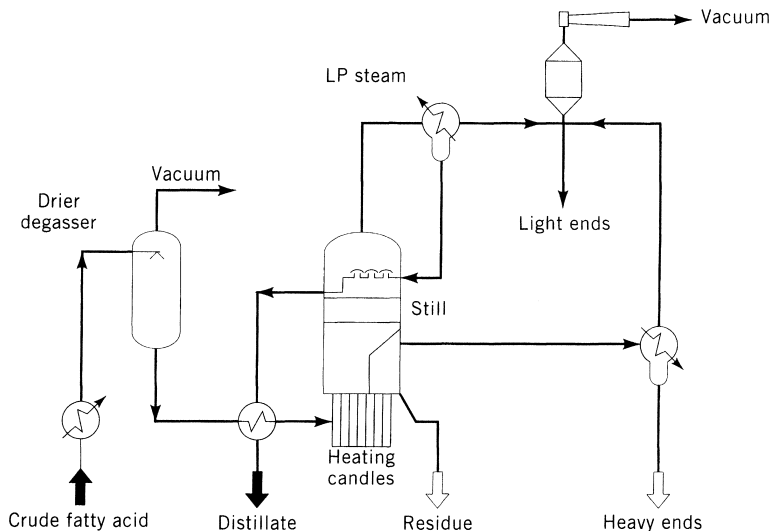


Figure 4. Lurgi's continuous fatty acid distillation (11).

Crude fatty acid is predried and degassed under vacuum and fed to the distillation unit, which is operated at a vacuum of 1.2 kPa or less and a temperature of approximately 200°C. Modern stills use thermal oil or high-pressure steam as the heat source. Stripping steam is provided to improve circulation and reduce partial pressure, thus lowering the temperature and reducing degradation losses. The steam facilitates the removal of low boiling impurities as well as odor and color bodies from the vapor exiting the system and from the light ends. The distilled fatty acid has an almost water white color and is free of the major impurities. The heavy ends consist of the higher boiling components, usually of lower quality, which can either be withdrawn separately or recycled directly for redistillation (11). The bottoms or residue are charred viscous polymerized material, which is disposed of by blending with heavy residual oil and used as boiler fuel. It may also find use as an asphalt additive.

Lurgi (11) establishes an approximate utility consumption per ton of crude fatty acid feed for plant sizes from 50 t to 200 t per day as follows:

Heating steam (5000 kPa)	370 kg
Steam (300–1000 kPa)	150 kg
Cooling water (20°C)	15 m ³
Electrical energy	5 kWh
Export steam (300 kPa)	120 kg

Fatty Acid Fractionation. Today's market is becoming more and more demanding. Specific fractions with purity in excess of 99% are in demand for special

products. Fortunately, developments in fractionation technology can now readily meet this challenge. Purities of 99.5% can be achieved for pure cuts of C12 or C14 fraction.

Fractionation makes it possible to separate the fatty acid mixtures into narrower cuts or even individual components. The detergent-grade feedstock C12–C18 fraction is separated from the whole cut by topping off the C8–C10 fraction. The middle cut, C12–C14, can be further fractionated from the C12–C18 cut through the use of multistage fractionation employing two or more columns.

All commercially available fractionation processes can give comparable performances. Basically, each process uses a deaerator, heat source, fractionation column, condensing system, and vacuum source. These processes may differ in the internals of the column, in the manner of evaporation and condensation, and in the piping arrangement for better heat recovery, but they can give equally good results.

The column internals are designed to provide intimate contact of the vapor and the distillate, together with the lowest pressure drop possible through the column. Various arrangements are employed, such as bubble caps, exchange trays, regular packings, or structured packings. Lurgi uses the Thorman tray, which claims high-separation efficiency, flexible loading, and long-term trouble-free operation. Structured packings, such as the Mellapak or Sulzer or the Glitch, are finding favor in modern columns. These packings are claimed to have high-separation efficiencies and minimal pressure drops of 10–50 Pa mbar per stage. As a result of their structure, there is little liquid holdup. Slight changes in operating parameters can easily upset the equilibrium conditions, and it is thus best to operate the column at steady conditions.

The vacuum system is provided independently for each column and usually consists of a mechanical vacuum pump and a steam ejector to achieve the highest vacuum. A centralized vacuum system is not recommended, as a process upset in one stage can readily affect the other stages. The heat source can be a shell-and-tube heat exchanger using thermal oil. Figure 5 shows a Lurgi fractionation system that has two columns to produce three separate fractions.

5. METHYL ESTERS

Fatty acid methyl esters play a major role in the oleochemical industry. Methyl esters have increasingly replaced fatty acids as starting materials for many oleochemicals. They are used as chemical intermediates for a number of oleochemicals, such as fatty alcohols, alkanolamides, α -sulfonated methyl esters, and many more. One other potential use of methyl esters is as a substitute for diesel oil (14). Methyl esters are clean burning with no sulfur dioxide emission. Although the heat of combustion is slightly lower, there is no engine adjustment necessary and there is no loss in efficiency.

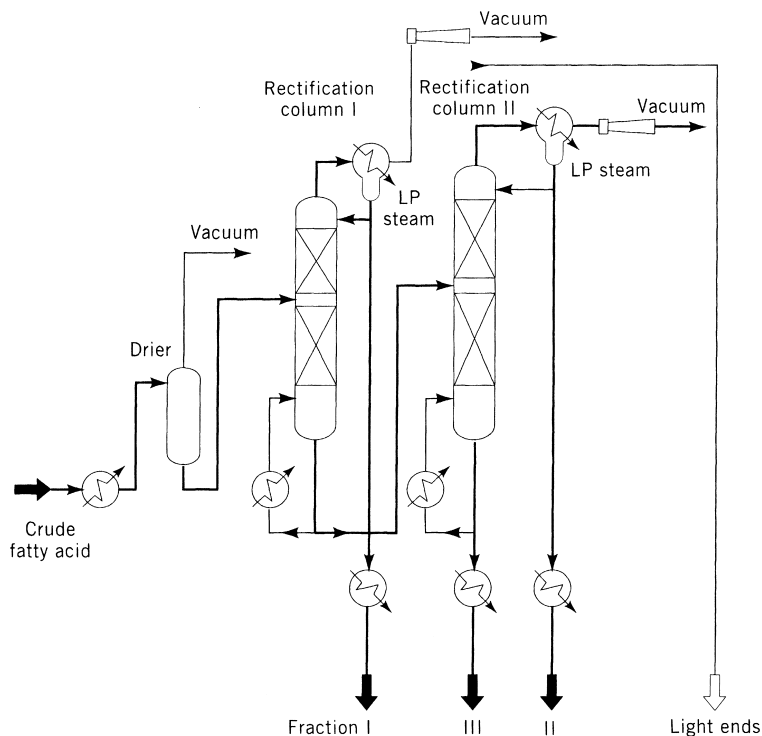


Figure 5. Fatty acid fractionation (11).

5.1. Advantages of Methyl Esters

The use of methyl esters instead of fatty acids as starting materials for many oleochemicals is rapidly gaining ground because of the following advantages (14):

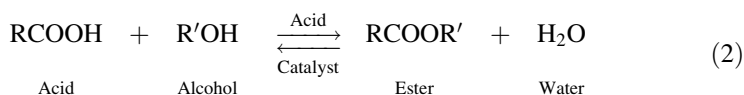
1. *Lower energy consumption.* The production of methyl esters requires much lower reactor temperatures and pressures than the splitting of fats and oils to obtain fatty acids.
2. *Less expensive equipment.* Methyl esters are noncorrosive and are produced at lower operating pressure and temperature conditions, hence they can be processed in carbon steel equipment; fatty acids are corrosive and require heavy-duty stainless steel equipment.
3. *More concentrated glycerine byproduct.* Transesterification is a dry reaction and yields concentrated glycerine, while fat splitting produces glycerine water, which has more than 80% water; thus, recovery of the latter uses more energy.
4. *Easier to distill-fractionate.* Esters are more easily distilled because of their lower boiling points and are more heat stable than the corresponding fatty acids.

5. *Superior to fatty acids as chemical intermediates in some applications.* In the production of alkanolamides, esters can produce superamides, with more than 90% purity against fatty acids, which can only produce amides with a purity of 65–70% amides.
6. *Easier to transport.* As a result of their chemical stability and noncorrosive property, esters are far easier to transport than fatty acids.

One major consideration is the need to recover and recycle the methanol. As methanol is a toxic and an explosive material, use of explosion proof equipment and extra safety precautions are mandatory.

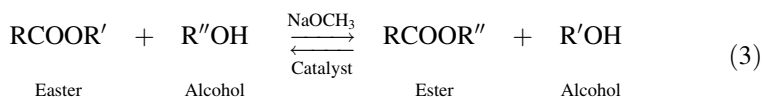
5.2. Chemistry of Esterification and Transesterification

Esterification. Esterification is the reaction of an acid with an alcohol in the presence of a catalyst to form an ester. The reaction is expressed by the general equation:



Generally, acid catalysts like sulfuric acid are employed. Esterification is a reversible reaction. Thus, water must be removed to drive the reaction to the right and obtain a high-ester yield.

Transesterification. Transesterification, on the other hand, is the displacement of the alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. This reaction, cleavage of an ester by an alcohol, is more specifically called alcoholysis and is represented by the general equation:

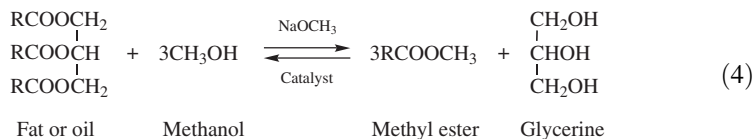


In this case, a new ester is formed. Generally, alkaline catalysts are used with sodium methylate said to be the most effective, although sodium hydroxide can also be used.

Transesterification is an equilibrium reaction. To shift the reaction to the right, it is necessary to use a large excess of alcohol or to remove one of the products from the reaction mixture. The second option is preferred where feasible, as in this way, the reaction can be driven to completion.

Transesterification is a general term. More specifically, if methanol is used, the reaction is termed *methanolysis*. Methanol is generally used because it is cheap, but other alcohols can be used.

The reaction with fats and oils and using methanol is represented by the general equation:



Although the equation reflects the overall reaction, the reaction usually consists of a series of consecutive reversible steps. The sequence of steps is triglyceride to diglyceride to monoglyceride with 1 mole of methyl ester formed at each cleavage (14).

The stoichiometry of the reaction requires 3 moles of methanol for each mole of triglyceride. When up to 100% excess methanol is used, the conversion rate is at its highest (14). The catalysts used are alkaline catalysts. Sodium methylate is commonly used, although KOH or NaOH are also used.

The conversion rate is also strongly influenced by the reaction temperature. However, given enough time, the reaction will also proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (14).

Impurities in the oil used also affect conversion rates. Under the same conditions, 67–84% conversion using crude vegetable oils can be obtained, compared with 94–97% when using refined oils (14). The free fatty acids in the original oils interfere with the catalyst. However, under conditions of high temperature and pressure, this problem can be overcome.

5.3. Methods of Manufacture

Methyl esters of fatty acids can be made either by esterification of the fatty acids or transesterification of the triglycerides using methanol.

Esterification Processes. There are two general methods used for esterification: the batch process and the continuous process. Esterification can be done batchwise under pressure at a temperature of 200–250°C. As it is an equilibrium reaction, the water is removed continuously to obtain a high-ester yield (15).

Henkel has developed a continuous countercurrent esterification using a double-plate reaction column. The technology is based on the principle of an esterification reaction with the simultaneous absorption of the superheated methanol vapor and desorption of the methanol–water mixture (15).

Figure 6 shows the Henkel continuous process of fatty acid esterification. The reaction is carried out at a pressure of approximately 1000 kPa and a temperature of 240°C. One advantage of this process is the excess methanol can be kept significantly lower at 1.5:1 molar ratio of methanol:fatty acid versus the batch process at 3–4:1 molar ratio. The methyl ester, having undergone distillation, does not require further refining. The excess methanol is rectified and reused (15).

The continuous esterification process is superior to the batch process, in that the same high yield can be obtained in a much shorter dwell time and with substantially

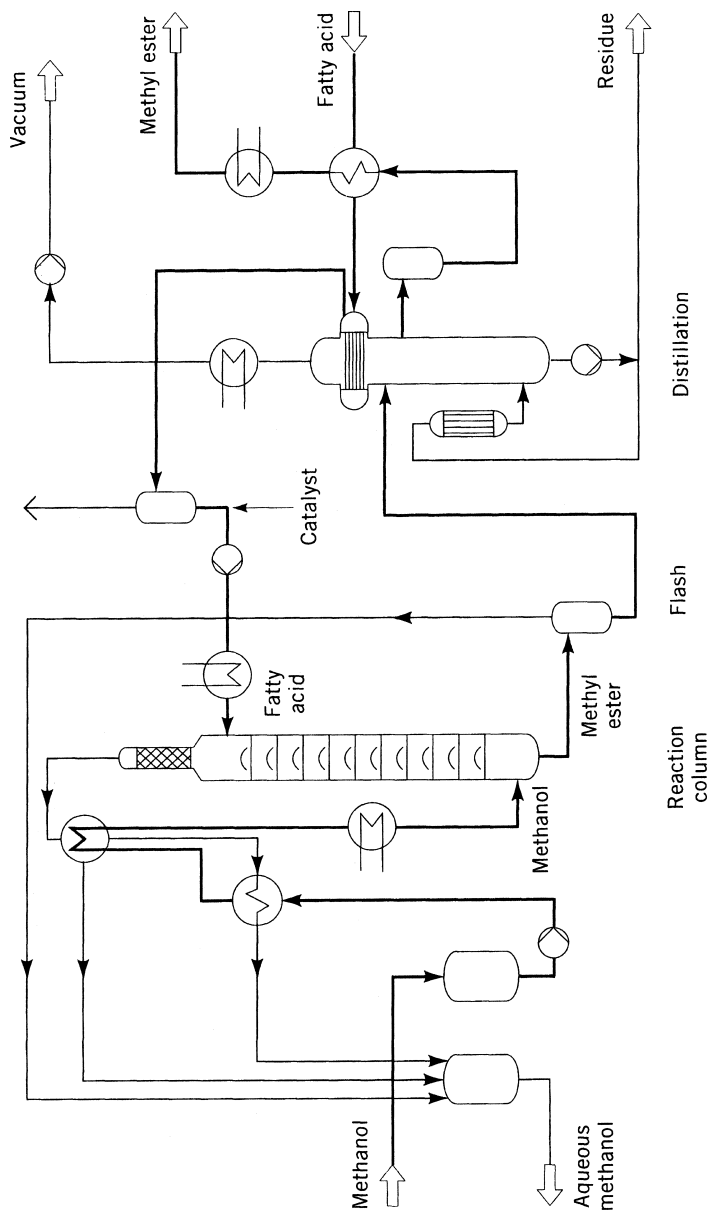


Figure 6. Manufacture of methyl esters by esterification (15).

less excess methanol. The esterification process is a preferred method for the production of esters from specific fatty acids (15).

Transesterification Processes. Transesterification of fats and oils is the most commonly used process for the manufacture of methyl esters, except in cases where methyl esters of specific fatty acids are needed.

Triglycerides can readily be transesterified batchwise at atmospheric pressure and at a slightly elevated temperature of approximately 60–70°C with an excess of methanol and in the presence of an alkaline catalyst. The mild reaction conditions, however, requires the removal of free fatty acids from the oil by refining or pre-esterification before transesterification. This pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240°C). Under these conditions, simultaneous esterification and transesterification take place (15). The mixture at the end of the reaction is allowed to settle. The lower glycerine layer is drawn off whereas the upper methyl ester layer is washed to remove entrained glycerine and is then processed further. The excess methanol is recovered in the condenser, sent to a rectifying column for purification, and recycled.

Continuous transesterification is well suited for large capacity requirements. Depending on the quality of the feedstock, the unit can be designed to operate at high pressure and high temperature or at atmospheric pressure and slightly elevated temperature.

Figure 7 shows a Henkel process flow diagram operated at 9000 kPa pressure and 240°C using unrefined oil as feedstock. Unrefined oil, methanol in excess, and catalyst are metered and heated to 240°C before feeding into the reactor. The bulk of the excess methanol is flashed off as it leaves the reactor and is fed to a bubble tray column for purification. The recovered methanol is recycled into the system.

The mixture from the reactor enters a separator where the glycerine in excess of 90% concentration is removed. The methyl ester is subsequently fed to a distillation column for purification. Further fractionation into special cuts may follow if desired (15).

Figure 8 shows a Lurgi process flow diagram operating at normal pressure. The process requires the use of a degummed and deacidified feedstock. The refined vegetable oil and methanol are reacted in a two-stage mixer–settler arrangement in the presence of a catalyst. The glycerine produced in the reaction, dissolved in the surplus methanol, is recovered in the rectification column. Most of the entrained methanol and glycerine are recovered from the methyl ester in the countercurrent scrubber. The methyl ester can be further purified by distillation (11).

5.4. Materials and Utilities Consumption Per Ton of Ester

Lurgi's (11) technical data for plant sizes of 30–250 tpd are as follows:

Methanol	142 kg
Refined PKO or CNO	995 kg

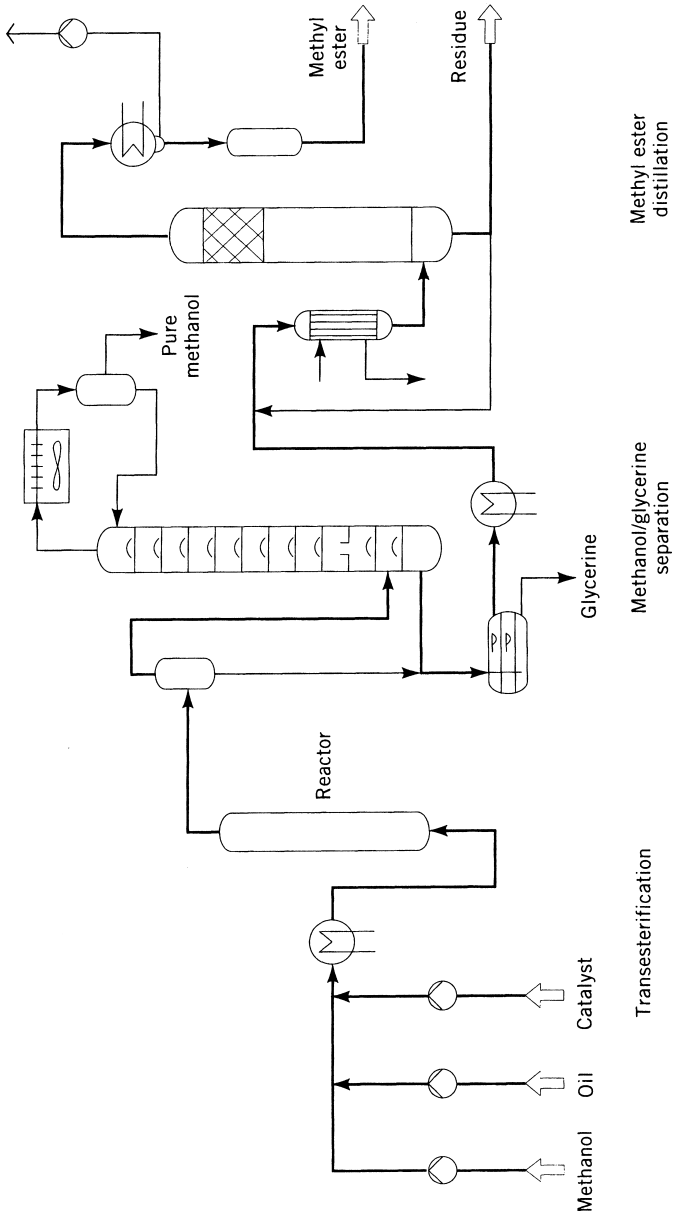


Figure 7. Manufacture of methyl ester by transesterification (15).

Steam (400 and 1000 kPa)	250 kg
Heat energy (thermal oil)	420,000 kJ
Cooling water (20°C)	25 m ³
Electrical energy	10 kWh

Lion Corporation of Japan developed a continuous transesterification process using unrefined feedstock known as the ES process. The free fatty acid in the oil is pre-esterified by passing the feedstock and methanol through a packed column of a special catalyst resin, after which transesterification is conducted through a two-stage reactor. A high conversion rate of more than 99% is claimed (16).

6. FATTY ALCOHOLS

Fatty alcohols make up one of the major basic oleochemicals enjoying a continuing growth rate. As a primary raw material for surfactants, its growth parallels increasing economic prosperity and improvement in the standard of living. Fatty alcohols are increasingly gaining favor as the surfactant raw materials of choice because of their biodegradability as well as availability from renewable resources.

Fatty alcohols can be produced from natural oils, or synthesized from petrochemicals. The current world supply of fatty alcohols is equally divided between natural and synthetic. However, the use ratio of natural: synthetics varies with each region. The overall world ratio is projected to go in favor of natural fatty alcohols. This can be attributed to the increasing supply and price stability of the lauric oils. The primary source of lauric oil is in the Southeast Asian region where most processing plants have been established.

6.1. Methods of Manufacture

The different methods used in the production of fatty alcohols from various sources are (1) hydrolysis of wax esters using animal fats, (2) sodium reduction process using fats and oils, (3) Ziegler process using ethylene, (4) oxo process using olefins, (5) catalytic hydrogenation of fatty acids and methyl esters from fats and oils, and (6) direct hydrogenation of fats and oils.

Although not applicable to coconut oil, a brief description of the first method is included for historical reference; brief descriptions of the second and sixth methods are also included. The third and fourth methods use raw materials of petrochemical origin and will not be discussed here. However, it should be mentioned again that approximately 50% of the world's supply of fatty alcohols is produced from these two methods. A more detailed discussion of the fifth method is given later.

Hydrolysis of Wax Esters. Fatty alcohol was first obtained from the hydrolysis of wax esters of animal origin, primarily spermaceti from sperm whale. With the worldwide ban on whale hunting, however, this source is no longer available.

Spermaceti wax is split by heating with concentrated sodium hydroxide above 300°C. The liberated alcohol, approximately 35% yield, is separated by vacuum

distillation from the soap and water formed. The product consists essentially of cetyl, oceryl, and arachidyl alcohols (5).

Sodium Reduction Process. In 1909, Beauvault and Blanc discovered the sodium reduction process of manufacturing fatty alcohols from coconut esters. Fatty alcohol plants established in the 1930s used this process. Although the basic process is relatively simple, actual plant operations in handling the reactants and products are much more complex. The hazards of handling metallic sodium is an additional factor that caused this process to gradually lose out to the catalytic hydrogenation process.

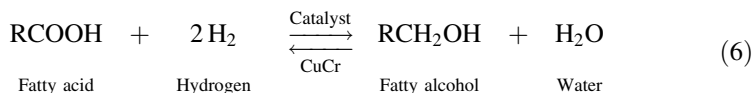
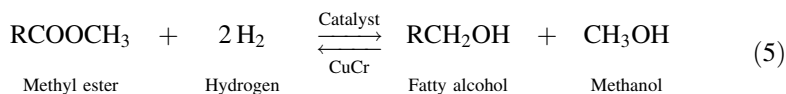
Direct Hydrogenation. A more recent process, developed and patented by Henkel KGaA, is the direct hydrogenation of natural oils or triglycerides. However, because of the severe conditions employed, a major portion of the valuable glycerine byproduct is also hydrogenated to lower valued propylene glycol and propyl alcohol. The loss of glycerine, the higher consumption of hydrogen gas, and increased use of catalyst do not justify commercial production as yet (15).

6.2. Fatty Alcohols from Natural Fats and Oils

The manufacture of fatty alcohols from natural oils can be made either through the methyl ester route or fatty acid route. These two methods are both well established and are strongly competitive with each other. Commercial plants around the world use either route. Figure 9 shows the manufacturing routes of fatty alcohols from natural fats and oils.

6.3. Chemistry of Hydrogenation

The hydrogenation of methyl esters and of fatty acids to form fatty alcohols is given by the following general equations.



The direct hydrogenation of fatty acids as shown in Equation 6 is not used in a large commercial scale due to the need for higher reaction temperatures resulting in lower yields, and to the damaging effects on the catalyst. Traditionally, the fatty acids are first converted to esters before hydrogenation (15, 17).

Lurgi (17) has managed to overcome this problem by simultaneous esterification of the fatty acid with the alcohol and the hydrogenation of the ester in the same reactor as given by the following equations:

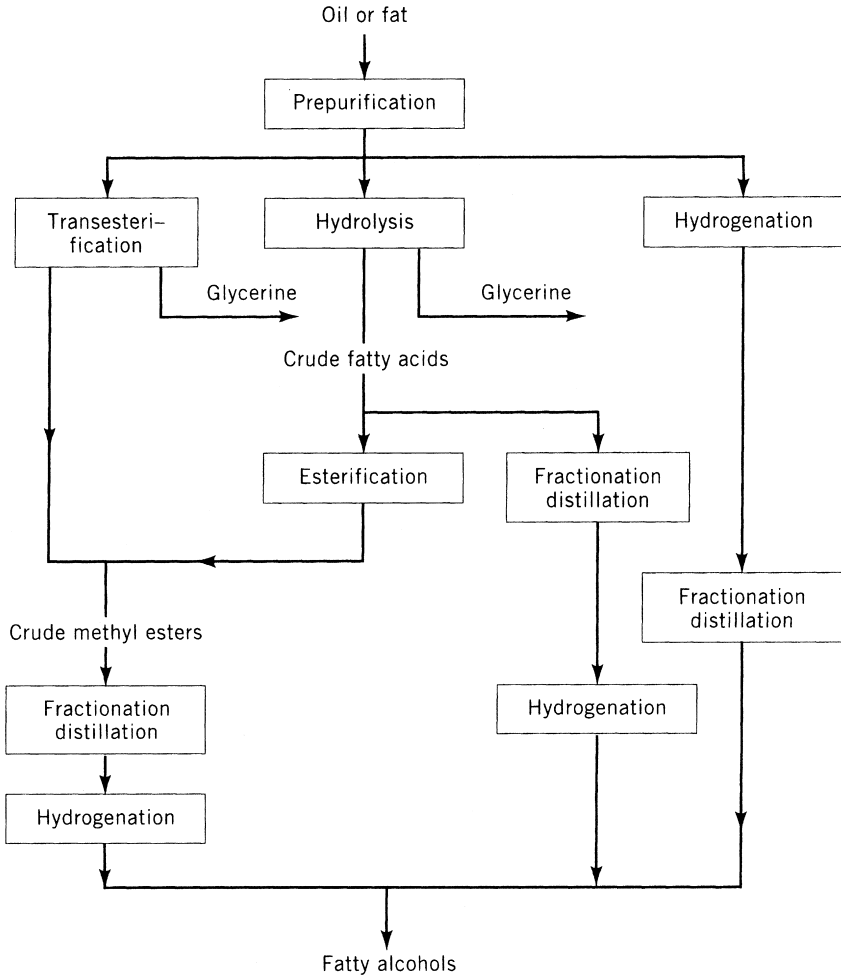
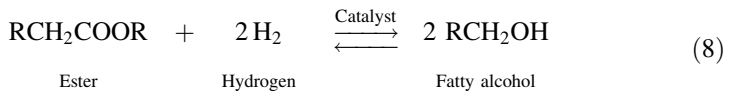
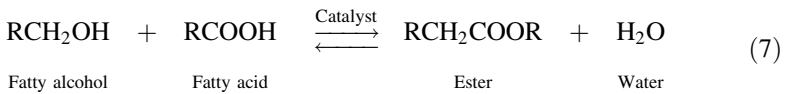


Figure 9. Manufacturing routes of fatty alcohols from natural fats and oils (15).



The fatty acids are introduced into a large volume of circulating fatty alcohols, more than 250 times the volume of the acids, so that the esterification is effected rapidly without the damaging effect of the fatty acids on the catalyst (17).

6.4. High-Pressure Hydrogenation Processes

The fractionated methyl esters can be converted into fatty alcohols by the high-pressure hydrogenation process in the presence of a catalyst. Usually, copper chromite catalyst is used. Copper chromite catalyst also converts any unsaturated carbon double bonds so that only saturated fatty alcohols are formed. If unsaturated fatty alcohols are desired, a special zinc-bearing catalyst is employed.

The hydrogenation process is carried out at 25,000–30,000 kPa and a temperature of 250–300°C in a tubular column. Depending on the method by which the catalyst is employed, the hydrogenation can be conducted using the suspension process or the fixed bed process.

Suspension Process. In the suspension process, the catalyst is slurried with a small amount of the methyl ester and then fed into the reactor together with the rest of the ester.

Figure 10 shows a simplified process flow diagram of the hydrogenation of methyl ester using the suspension process. The methyl ester and hydrogen gas are preheated separately. The copper chromite catalyst is pre-slurried in a small amount of methyl ester and is introduced simultaneously with the preheated methyl ester and hydrogen gas into the base of a tubular reactor (without packing). The catalyst is metered into the system in an amount of at least 2.0%. Approximately 20 moles of hydrogen gas per mole of ester feed are used. The hydrogen gas, bubbling through, serves also to agitate the reactants.

The reaction is conducted at approximately 25,000–30,000 kPa and 250–300°C. As hydrogenation is an exothermic reaction, care must be taken to control the reaction temperature to minimize side reactions leading to the formation of undesirable hydrocarbons. From the column, the reaction mixture is cooled, separating the hydrogen gas from the alcohol–methanol mixture. The hydrogen gas is recycled, and the alcohol–methanol mixture goes to the methanol-stripping unit where, at lower pressure, the methanol is stripped off, recovered, and recycled to the esterification or *trans*-esterification section. The crude fatty alcohol is filtered to separate the catalyst. A major portion of the catalyst is recycled, so that the consumption averages 0.5–0.7% of the alcohol produced.

The filtered alcohol is subsequently treated with caustic soda to form soap with any unreacted ester. The alcohol is finally distilled to strip off any hydrocarbons formed, which amount to about 2–3%. The soap remains in the still bottoms (15).

Fixed Bed Process. The fixed bed process, as differentiated from the suspension process, has the catalyst “fixed” as a bed inside the reactor. The catalyst is either compact pelletized or supported on a carrier. Figure 11 is a simplified process flow diagram for the hydrogenation of methyl esters using the fixed bed process.

The reaction is conducted in the vapor phase where a part of the organic feed is vaporized in an excess of hydrogen gas (20–25 moles) through a peak heater before passing through the fixed catalyst bed. The hydrogenation is carried out at 20,000–30,000 kPa and 200–250°C. The reaction mixture leaving the reactor is cooled and is separated into the gas and liquid phases. The gas phase, mostly excess hydrogen,

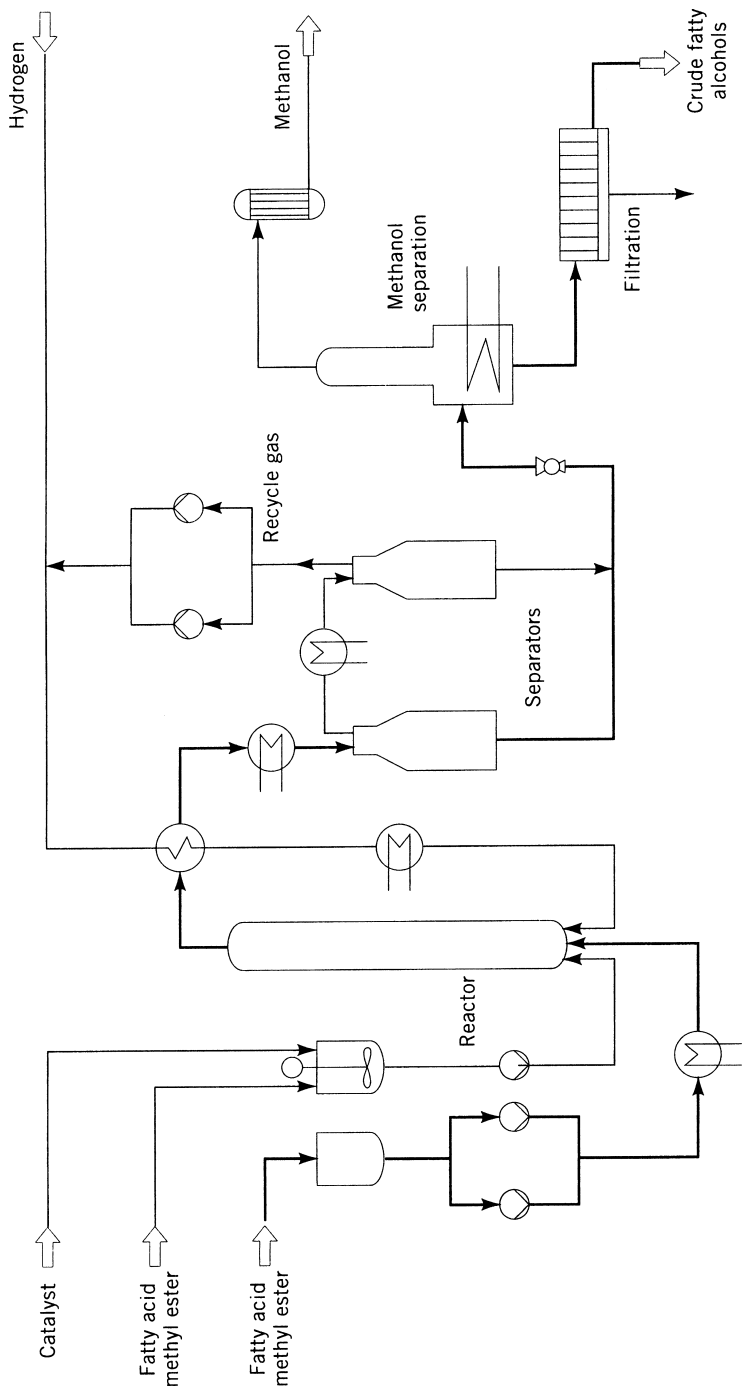


Figure 10. High-pressure hydrogenation of fatty acid methyl esters—suspension process (15).

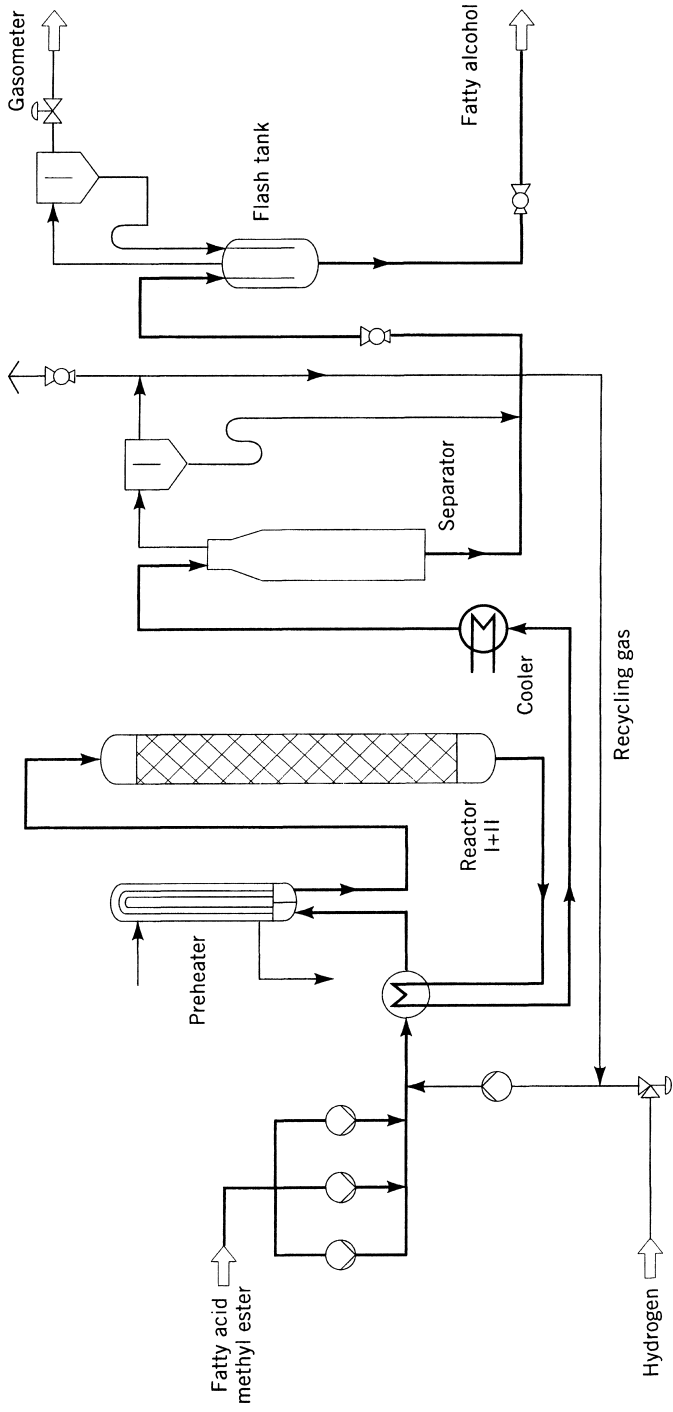


Figure 11. High-pressure hydrogenation of fatty acid methyl esters—fixed bed process (15).

is recycled. The liquid phase is expanded into a flash tank to strip off the methanol from the fatty alcohol.

The operating conditions are comparatively mild, so that the fatty alcohol produced does not require further processing. The overall yield is 99% with hydrocarbons and unreacted ester not exceeding 1.0%. Catalyst consumption is claimed to be below 0.3% (15).

The Suspension Process Versus the Fixed Bed Process. The fixed bed process requires a somewhat higher capital investment, as it needs larger reaction vessels, gas recirculation pumps, and pipe work due to the higher volume of hydrogen gas used. The suspension process, on the other hand, requires additional equipment for the separation of catalyst, distillation of the crude fatty alcohol, and rework of the unreacted methyl ester.

In terms of raw materials consumption, the fixed bed process has a higher yield and the catalyst consumption is only half as much. The fatty alcohol via the fixed bed process has a higher quality. However, the quality of the fatty alcohol via the suspension process can also be brought up to the same level by further distillation (15).

6.5. Lurgi Fatty Acid Hydrogenation Method

The Lurgi method, which is a suspension process, makes possible the direct hydrogenation of fatty acids to fatty alcohols overcoming the damaging effects of the fatty acids on the copper-bearing catalyst. This is achieved by a two-step reaction. The first reaction is the esterification of the fatty acid with the fatty alcohol to yield the ester and water. The second reaction is the hydrogenation of the ester formed to produce 2 moles of the alcohol. Both reactions occur simultaneously in the same reactor. The large volume of the fatty alcohol recirculated, more than 250 times the fatty acid feed, effectively dilutes the feed, thus providing for an optimum condition for rapid and complete esterification (17). Figure 12 is a simplified process flow diagram of the Lurgi method of converting fatty acids to fatty alcohols.

The hydrogenation takes place inside the high-pressure reactor where the preheated materials—fatty acid feed, recirculated fatty alcohol with the slurried catalyst, and hydrogen gas—are fed continuously. The reaction is carried out at approximately 30,000 kPa and 280°C. The heat of the product mixture leaving the reactor is recovered by the recirculating hydrogen gas through the heat exchanger, after which the products are separated through a two-stage cooling–expansion system.

The gas phase (essentially excess hydrogen gas, some low boiling alcohols, and reaction water) is separated from the liquid alcohols in the hot separator. This mixture is cooled further in the cold separator, where the low boiling alcohols and reaction water are condensed and separated. The excess hydrogen gas is recycled into the system.

The liquid alcohols from the hot separator are pumped into a flash drum where the dissolved hydrogen is released and recycled with the make up hydrogen. The catalyst is separated from the crude fatty alcohol using a centrifugal separator. Part of the catalyst is replaced with fresh catalyst to maintain the activity and is

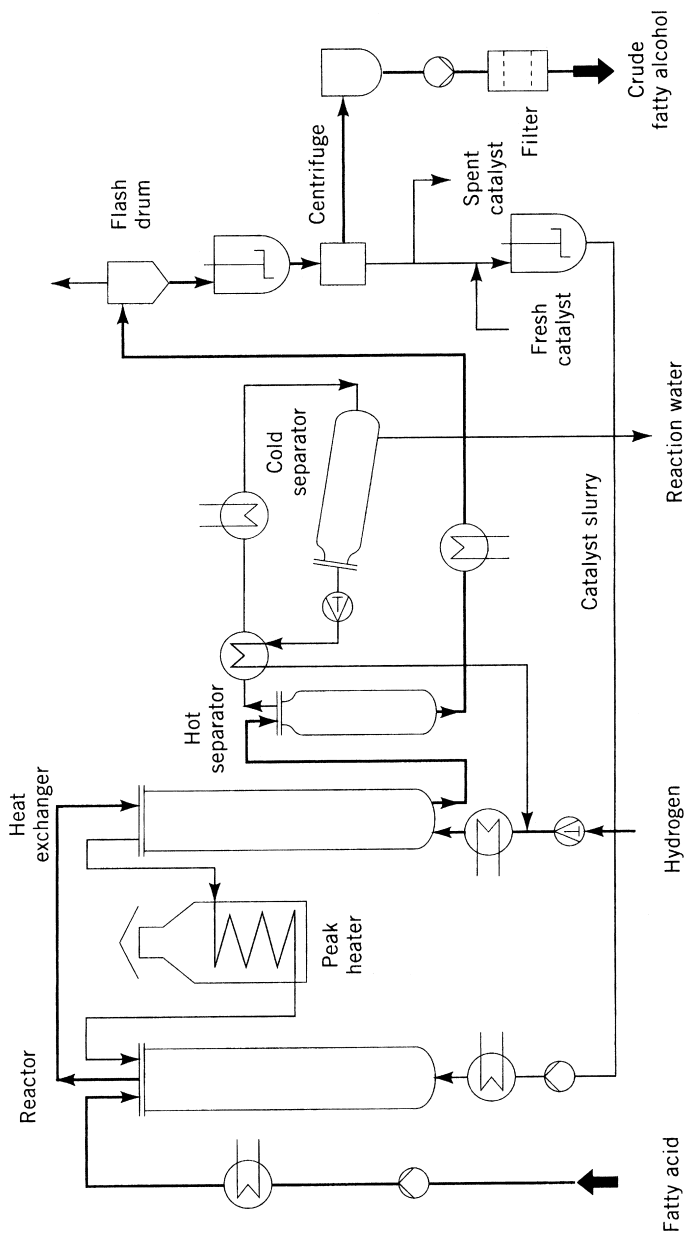


Figure 12. Fatty alcohol synthesis via hydrogenation of fatty acids (18).

recirculated with the fatty alcohol. The clear phase portion from the centrifugal separator is passed through a polishing filter to remove all traces of suspended solids. The resulting crude alcohol undergoes further distillation to remove hydrocarbons and may undergo fractionation if desired (18).

6.6. Materials and Utilities Consumption Per Ton of Crude Fatty Alcohol

Technical data for plant capacities of 50+ t/day are (11) as follows:

Distilled coco fatty acid	1050–1100 kg
Steam (ca. 15 bar)	170 kg
Cooling water (20°C)	27 m ³
Electric energy	130 kWh
Fuel gas	1.1×10^6 kJ
Catalyst (copper chromite)	5 kg
Hydrogen (0°C, 100 kPa, depending on hydrogen purity and fatty acid specification)	230–300 m ³
Boiler feed water	185 kg
Export steam (ca. 4 bar)	120 kg

Material Balance. Figure 13 shows the overall material balance for the manufacture of 1000 MT of distilled fatty alcohol starting from distilled coco fatty acids.

6.7. Fractionation of Fatty Alcohols

Crude fatty alcohol resulting from the various hydrogenation processes described previously may undergo fractionation to produce different cuts of alcohol. Figure 14 shows a flow diagram for the fractionation of crude fatty alcohols.

7. GLYCERINE

Glycerine is a tribasic alcohol occurring in nature in the form of triglycerides, which are glyceryl esters of fatty acids. All fats and oils are made up of triglycerides. Coconut oil contains approximately 13.5% glycerine, the highest among commercial fats and oils. The glycerine contents of other fats and oils range from 9 to 12%.

Glycerine is an important high-value byproduct obtained from the processing of fats and oils. It can also be synthesized from petrochemicals. However, with the increasing output of vegetable fats and oils worldwide, glycerine, from this latter source, plays a significant role in the world supply of this material. The production of glycerine from petrochemicals will not be discussed here.

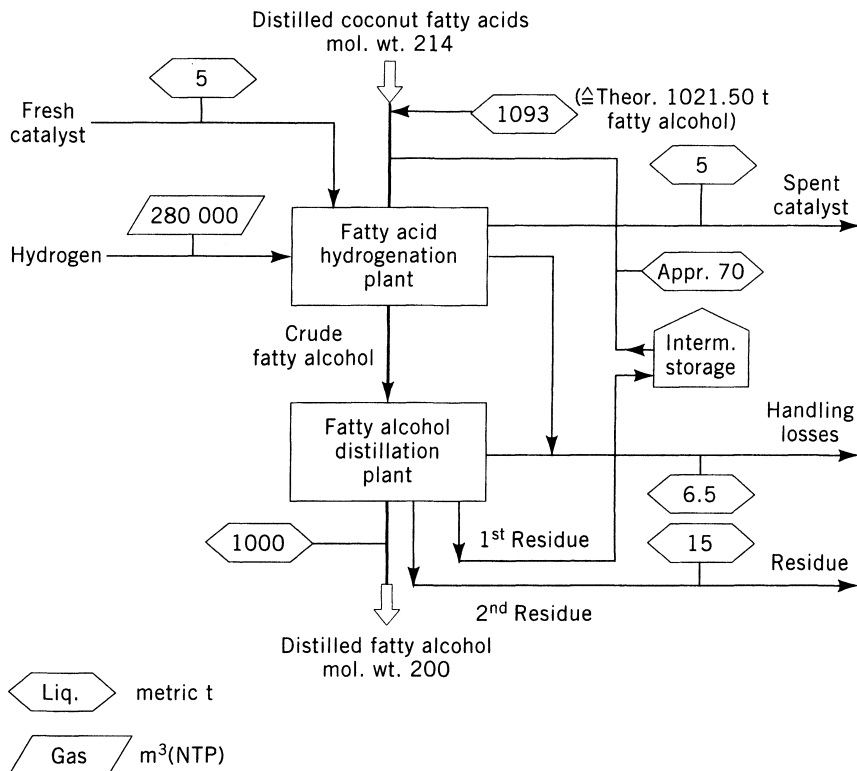


Figure 13. Overall material balance for the manufacture of 1000 MT distilled fatty alcohol from distilled coconut fatty acids (18).

7.1. Glycerine from Fats and Oils

Glycerine is obtained by cleavage of triglycerides using several methods:

1. Saponification of fats and oils using caustic soda to form soap and glycerine.
2. Splitting or hydrolysis of fats and oils in the presence of a catalyst to produce fatty acids and glycerine; the sweetwater formed contains 16–20% glycerine.
3. Transesterification, which results in the displacement of the glycerine from triglycerides when fats and oils are reacted with methanol in the presence of a catalyst to produce methyl esters; in this process, glycerine concentration in excess of 90% can be obtained because this is basically a dry reaction.

Both splitting or hydrolysis and transesterification were discussed earlier; therefore, only saponification will be covered briefly in this section.

Saponification. When fats and oils are saponified with caustic soda, the reaction is represented by the following equation:

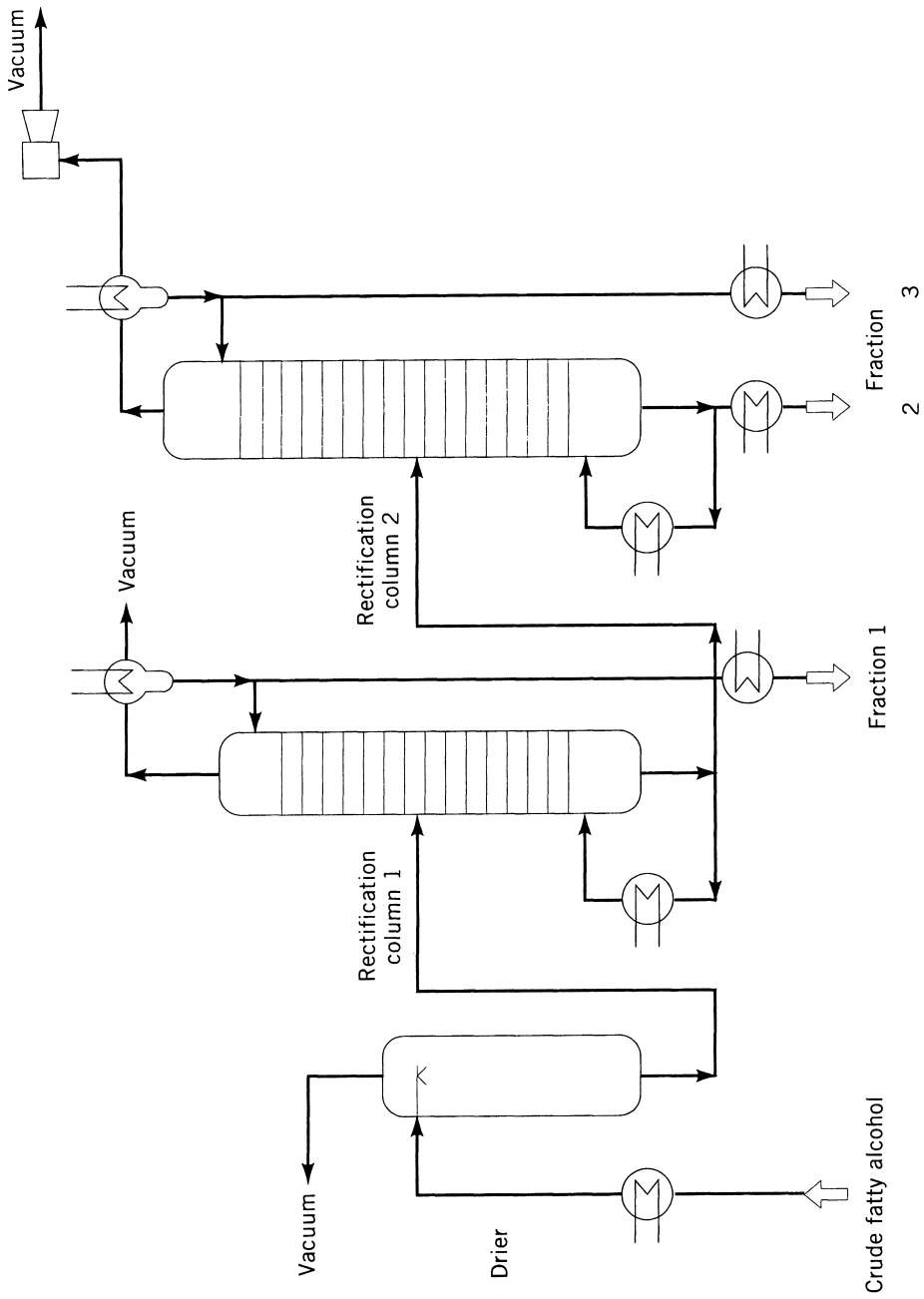
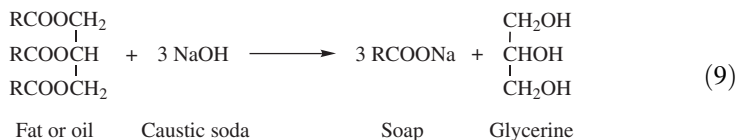


Figure 14. Fractionation of fatty alcohol (18).



Saponification yields soap and spent soap lye containing 8–12% glycerine.

Fats and oils can be saponified via the full-boiled process. The saponification process can be briefly described as follows. A refined blend of fats and oils is charged into a kettle and a predetermined amount of soap lye with sufficient concentrations of caustic soda, and salt is added. The mixture is boiled vigorously, using closed steam coils, until saponification is almost complete. The amount of caustic soda added is deliberately made less than the stoichiometric requirement, to ensure that the spent soap lye containing the glycerine has minimum alkalinity. The caustic soda in the spent soap lye is neutralized during subsequent treatment of the latter.

The salt used in the lye is necessary to keep the soap in the grained state and to facilitate the separation of the soap and the spent lye. The latter is drawn off after settling and transferred to the glycerine-processing section. Meanwhile, the soap undergoes further boiling and countercurrent multiple washing to complete the saponification and recover as much glycerine as possible before being finished to neat soap.

Continuous soap boiling, which is widely practiced, makes use of multiple washing columns or centrifuges. The objective is to effect optimum glycerine recovery with less lye bulk.

7.2. Methods of Purification

The glycerine obtained as a byproduct from the three processes noted above contains impurities and must undergo further processing to purify and concentrate it. Commercially, there are two known processes in use:

1. The conventional method of purification of the spent soap lye or sweetwater by acid–alum or ferric chloride treatment followed by evaporation, distillation, deodorization, and bleaching.
2. The ion exchange method of purification followed by evaporation and polishing.

Conventional Method. The conventional method is widely popular. Several manufacturers of equipment using this method are established worldwide. Among these are Lurgi and Feld & Hahn from Germany, Wurster & Sanger and Badger from the United States, and C.M.B. (Ballestra) and Mecchaniche Moderne from Italy. Figures 15–18 show some glycerine processing flow diagrams.

Basically, the steps used to produce high-grade glycerine with up to 99% purity are essentially the same. The spent soap lye, or sweetwater, is acidified with mineral

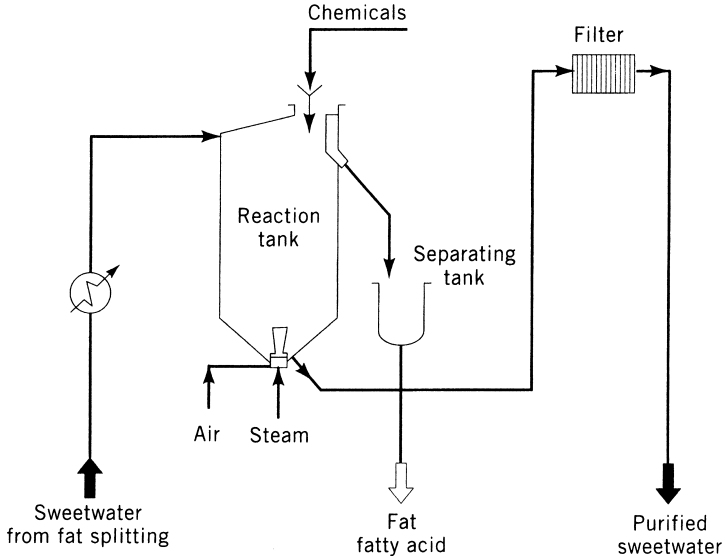


Figure 15. Sweetwater purification (batch) (11).

acid to split any dissolved soap and release it as fatty acid, which is skimmed off. The pH is adjusted, and alum or ferric chloride as a flocculant is then added to entrap the impurities, after which the mixture is filtered. The filtered lye is adjusted to a pH of 6.5 or higher before it is fed to the evaporator.

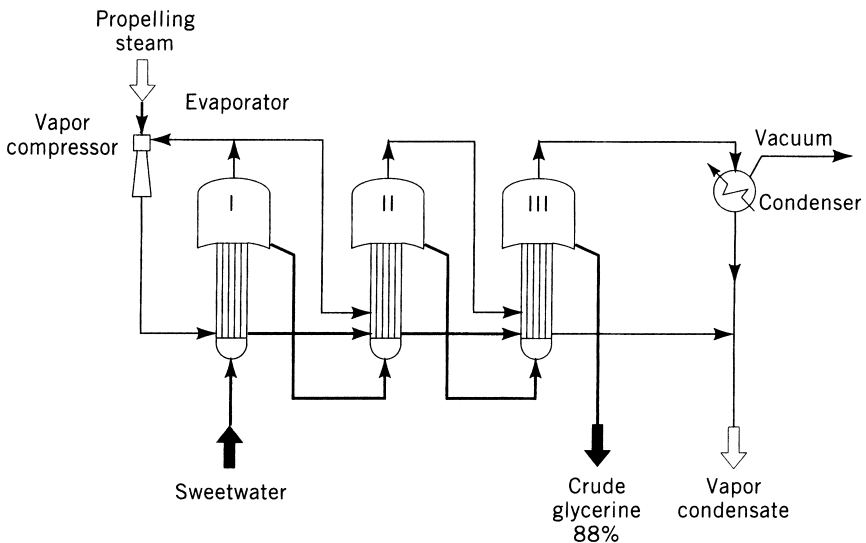


Figure 16. Sweetwater evaporation (triple effect with vapor compression) (11).

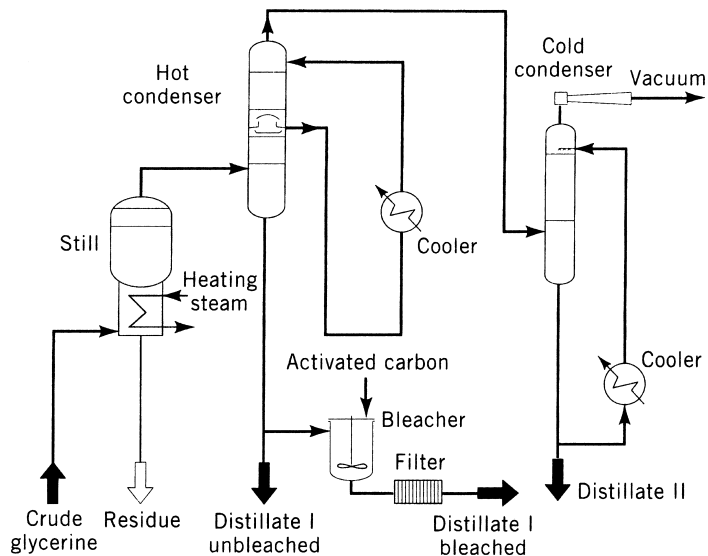


Figure 17. Glycerine distillation and bleaching (11).

The type of evaporator, either single or multiple effect, depends on the volume of materials to be processed. The crude glycerine obtained after evaporation has a concentration of 80–88% and undergoes further processing. Salt, which separates out during the evaporation of treated glycerine soap lye, accumulates in a salt pot positioned underneath the evaporator. The salt is recovered and recycled to the soap-making section.

The crude glycerine from the evaporator is distilled under a high vacuum of 660–1330 Pa absolute. Live steam is injected during distillation to keep the distilling temperature below 200°C. This is done to prevent the polymerization and decomposition of glycerine, which start at 204°C. Controlled condensation of the vapor separates the glycerine from the water vapor.

The condensed glycerine, with up to 99% purity, undergoes deodorization by blowing steam into it in a deodorization vessel under high vacuum. The glycerine is finally bleached with activated carbon and filtered to yield pharma-copoeia-grade glycerine with a purity of 99+%. Lower quality distillate near the tail end run is collected and sold separately as technical-grade glycerine.

Ion Exchange Method. The ion exchange method of glycerine purification is gaining wide acceptance because of the simplicity of operations and low energy consumption. This method is made possible by the availability of suitable ion exchange resins and is particularly suitable for refining of glycerine obtained from fat splitting or from transesterification, which is practically salt free. When salt is high, as in the spent lye from saponification, pretreatment to remove the salt is necessary.

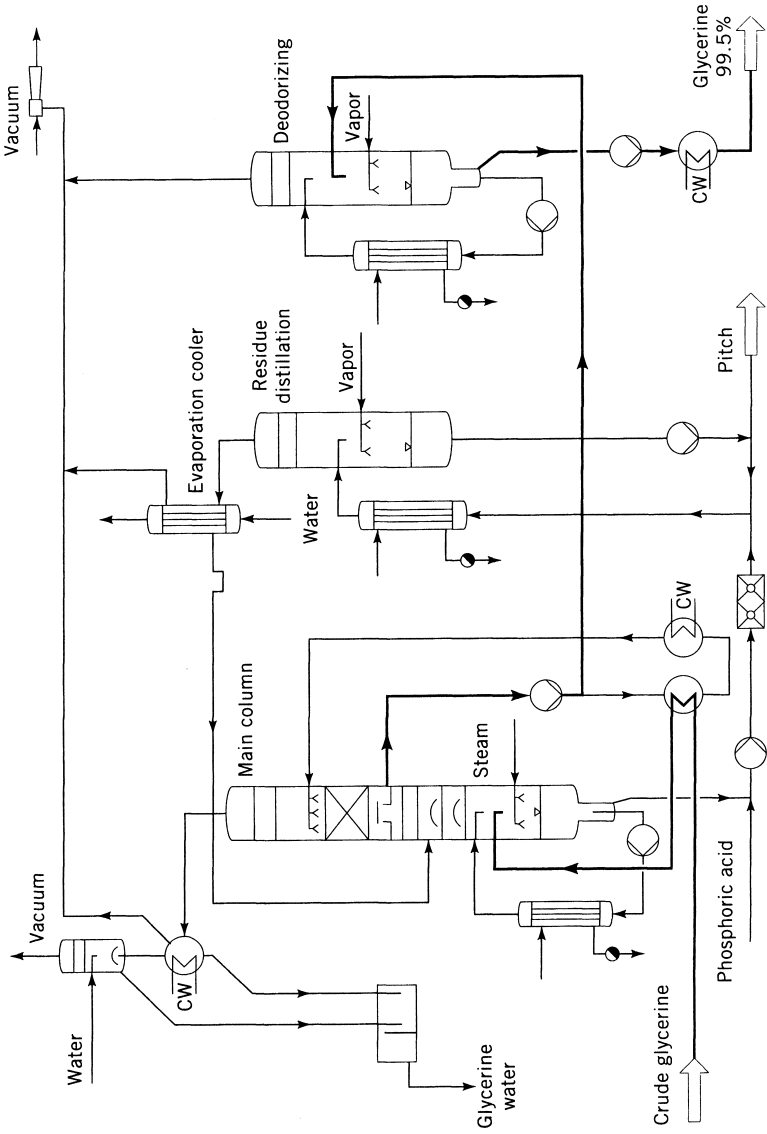


Figure 18. Glycerine distillation, Wurster & Sanger.

Purification by ion exchange involves the passage of the prefiltered material through successive beds of a strong cation, a weak anion, and a mixed bed of strong cation–anion resins. The ion exchange units operate efficiently with dilute solutions containing 25–40% glycerine.

Several resins are available commercially. Rohm and Haas has Amberlite 1R 120 or IRA 900 or Duolite C20 as strong cation; IRA 93SP or Duolite A 378 as weak anion; and the mixed bed polishing resins C20 MB and A 101D as strong cation–strong anion (19). Bayer, Germany supplies Lewatit S100, MP 64, and MP 500 resins for glycerine purification.

Passage through the resin beds eliminates traces of free fatty acids, color, odor bodies, and other mineral impurities present. Subsequent concentration of the purified glycerine solution is through evaporation using multiple-effect evaporators to produce glycerine with a purity of more than 99%. Final decolorization by passage through an activated carbon bed or treatment with activated carbon followed by filtration yields pharmaceutical- or C.P.-grade glycerine. Figure 19 shows a flow sheet for the ion exchange method of purifying glycerine.

Conventional Method Versus Ion Exchange Method. The conventional method offers greater flexibility but uses more energy, considering that much water must be evaporated and that the glycerine is distilled at a higher temperature. The ion exchange method requires less energy but cannot be used for sweetwater containing high chlorides. Chlorides foul up the ion exchange resin.

8. MONOALKYL PHOSPHATES

Monoalkyl phosphate and phosphate esters are special types of phosphorus-containing anionic surfactants that are of great industrial importance. They are used for flameproofing, as antistatic for textiles, for foam inhibition, as an extreme pressure (EP) lubricant additive, as a surfactant component for alkaline, and as acid cleaners and for special cosmetic preparations (5). The commercially available phosphate ester products are complex mixtures of monoester and diester, free phosphoric acid, and free nonionic.

8.1. Chemistry of the Reaction

Phosphate esters are prepared by the partial esterification of fatty alcohol with phosphorous oxychloride followed by hydrolysis (20). This method yields a product that is a mixture of monoalkyl, dialkyl, and trialkyl phosphates.

Another method of preparing alkyl phosphate is by reacting the fatty alcohol either with phosphorous pentoxide or with polyphosphoric acid. As shown by analysis of experimental results, the composition of alkyl acid phosphates differs significantly, depending on which of the two phosphating agents is used. The use of polyphosphoric acid leads to a higher monoester: diester ratio than that obtained with phosphorous pentoxide. Typical composition of the reaction products are given

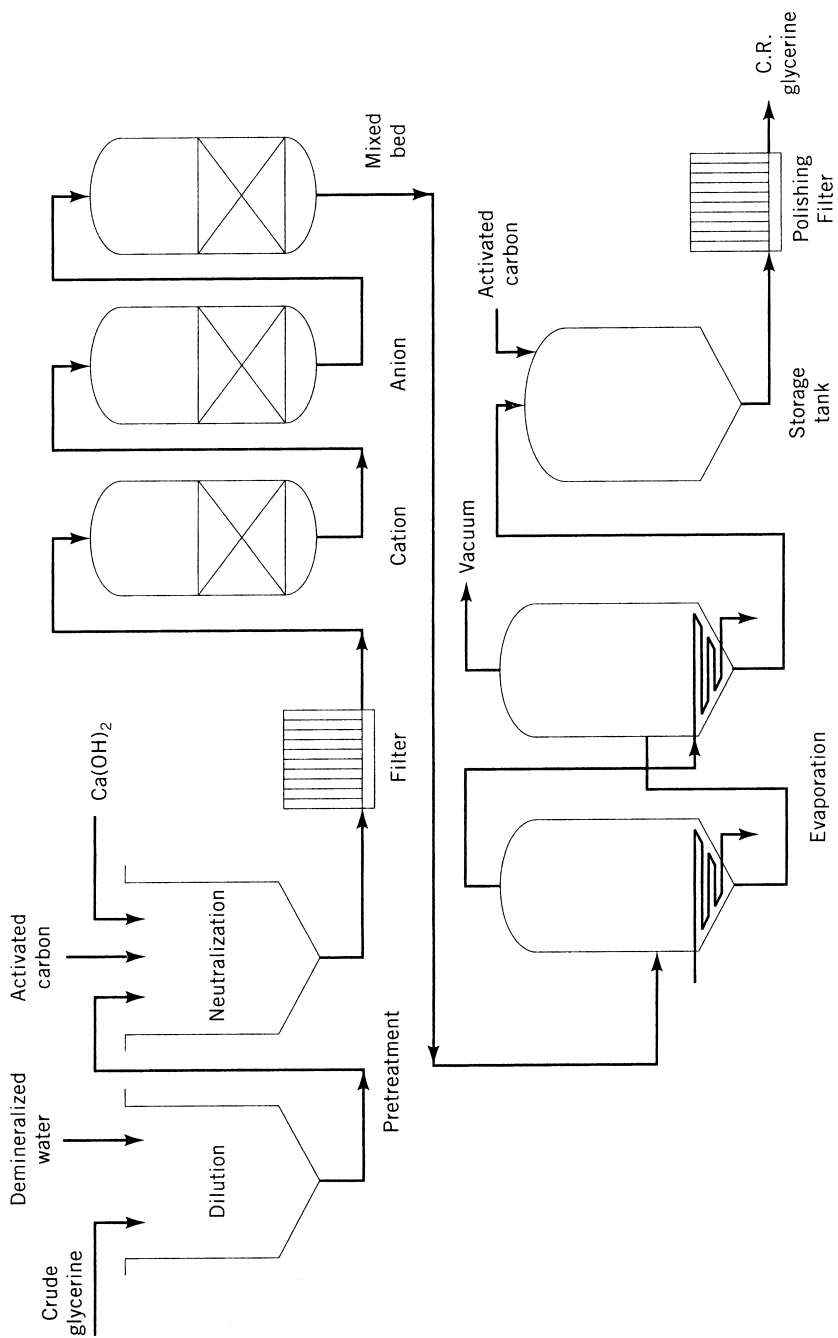


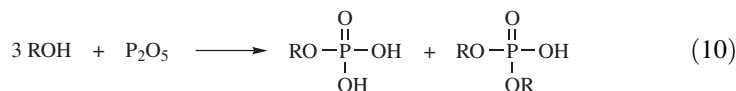
Figure 19. Ion exchange method of glycerine purification.

TABLE 3. Typical Composition of the Phosphate Ester Reaction Products (21)

Route	Components	Formula	Quantity (%)
Polyphosphoric acid	Monoalkyl phosphates	$\text{O}=\text{P}(\text{OH})_2 \text{OR}$	74
	Dialkyl phosphate	$\text{O}=\text{P}(\text{OR})_2 \text{OH}$	2
	Orthophosphoric acid	$\text{O}=\text{P}(\text{OH})_3$	10
	Free alcohol	ROH	14
Phosphorous pentoxide	Monoalkyl phosphate	$\text{O}=\text{P}(\text{OH})_2 \text{OR}$	35
	Dialkyl phosphate	$\text{O}=\text{P}(\text{OH})_2 \text{OH}$	42
	Orthophosphoric acid	$\text{O}=\text{P}(\text{OH})_3$	1
	Free alcohol	ROH	22

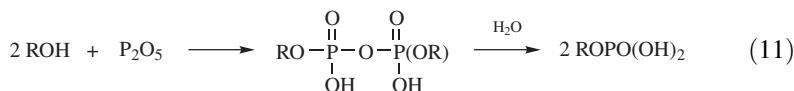
in Table 3. The difference in composition of the phosphate product also results in different properties and industrial applications.

Alkyl phosphates are more easily prepared by the addition of phosphorous pentoxide to fatty alcohols or fatty alcohol ethoxylates.



The resulting product is a mixture of dialkyl and monoalkyl phosphate esters. These products also contain small amounts of condensed phosphates and phosphoric acid. Neutralization of the acids with bases like alkali hydroxides, ammonia, or amines produces water-soluble anionic surfactants and emulsifiers.

The presence of water in the fatty alcohol or in the pentoxide increases the percent of monoalkyl acid phosphate. The use of higher molecular-weight fatty alcohols also increases the monoalkyl acid phosphate content. Products containing higher amounts of monoalkyl acid phosphate can also be derived from the reaction of 2 moles of fatty alcohol with 1 mole of phosphorous pentoxide. This reaction gives a high-yielding dialkyl pyrophosphate product, which is readily hydrolyzed to give an end product with a higher monoalkyl acid phosphate content than that obtained from the 3 : 1 ratio of alcohol to pentoxide (20).



8.2. Method of Manufacture

Phosphate esters are prepared at reaction temperatures from 80°C to 120°C at essentially atmospheric pressure. It has been claimed that temperature may be maintained at 30–80°C. Lower temperature favors lower color of the product (22), whereas, at temperatures near 100°C, noticeable decomposition occurs (23).

The phosphorous pentoxide is added portionwise to the alcohol at a rate such that the pentoxide dissolves and reacts without lumping. Lumping makes complete dissolution difficult and the P_2O_5 unreactive. The reaction between the alcohol and the P_2O_5 is carried out in the liquid phase and is basically exothermic. No catalyst is required. The addition of a small amount of hypophosphorous acid or its salt gives a colorless, color-stable product.

8.3. Properties and Uses

Monoalkyl phosphates inhibit the foam generation of other anionic and nonionic surfactants. The composition of the phosphate ester greatly affects the functional properties of the product.

Most phosphate esters are pale yellow to amber in color, sweet smelling, viscous liquid, or pastes. Depending on the type of phosphate esters, they have many important properties, among which are wetting, detergency, solubilizing, emulsification, surface tension reduction, foaming, dedusting, lubricity, antistatic, corrosion inhibition, chelating, dispersing, and antisoil redepositing agent (23). They have been proven to be extremely useful in a variety of applications where alternative anionic, nonionic, or amphoteric surfactants fail to give the desired functional properties.

Phosphate esters possess strong tolerance to electrolytes and alkalis. Their wetting properties are independent of the pH and, therefore, are used as surfactant components in both alkaline and acid cleaners (5). Their detergent properties are considered equal to nonionic surfactants, and they have excellent temperature stability. In their acid form, phosphate esters are moderately strong acids and, when neutralized to pH 5–8, have low order of toxicity. Phosphate esters are considered to be hydrotrope agents and are biodegradable.

9. ALKANOLAMIDES

Alkanolamides are condensation products of the reaction of a primary or a secondary alkanolamine with a fatty acid, a methyl ester, or a triglyceride such as coconut oil. The composition and functional properties of alkanolamides vary considerably, depending on the reactants employed and the reaction conditions. Such properties include superfatting, wetting, foam boosting, foam stabilizing, thickening, lubricating, emolliency, skin protection, emulsifying, and corrosion inhibition.

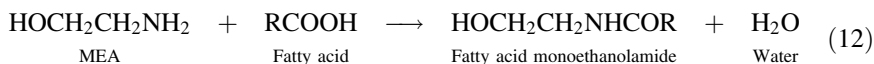
Alkanolamides are nonionic surface active agents that find application in a multitude of uses. There are four major groups of fatty alkanolamides: (1) monoethanolamides (MEA), (2) diethanolamides (DEA), (3) monoisopropanolamides (MIPA), and (4) ethoxylated or PEG alkanolamides. Each group has its own specific functions and uses in formulations.

Early experiments in the preparation of alkanolamides were begun by Kritchevsky (24, 25). It involves condensation reactions of fatty acids, triglycerides, esters, amides, anhydrides, and halides with an alkanolamine. The reaction was carried out at 100–300°C at atmospheric pressure. An important improvement was made by

Meade (26), who made use of an alkali metal alkoxide as a catalyst at 100°C at atmospheric and slightly above atmospheric pressure. Further refinement was made by Tesoro (27), who conducted the reaction at 55–75°C and a vacuum of 4–8 kPa. Schurman (28) patented a continuous process for making alkanolamide, which makes use of a thin film reactor. It is claimed the short contact time in the reactor produces a high-purity alkanolamide (29).

9.1. Chemistry of the Reaction

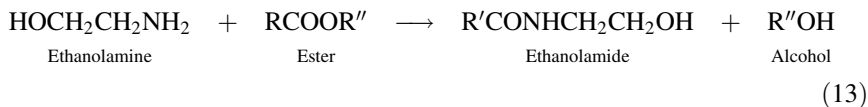
Reaction with Fatty Acids. When alkanolamines react with fatty acids in the ratio of 1 : 1 at 140–160°C, *N*-alkylolamides are formed.



The reaction is a two-stage reaction with the initial formation of the alkanolamine soap followed by dehydration to form the alkanolamide. At the same time, significant quantities of amine esters and amide esters are formed by the side reaction. If a dialkanolamine is used as the starting material, smaller amounts of amine diester and amide diester are formed as well as some morpholine and piperazine derivatives.

Reaction of dialkanolamines with fatty acids in a 2 : 1 ratio at 140–160°C gives a second major type of alkanolamide. This product, in contrast to 1 : 1 alkanolamide, contains a considerable amount of unreacted dialkanolamine, which accounts for the aqueous solubility of the product.

Reaction with Esters. The reaction of an ester, such as cocomethyl ester, with an alkanolamine at 110°C produces an *N*-alkylolamide.



The reaction of methyl esters of fatty acids with alkanolamines is used commercially to prepare high-purity 1 : 1 alkanolamide. This product, in contrast to the 1 : 1 alkanolamides prepared from the parent fatty acids, contains only a small quantity of the byproducts or unreacted starting material.

There are two competing reactions: amide formation and transesterification. The most desirable reaction is one that gives the highest amide ester byproduct. For the yield of the amide to exceed 90%, reduced pressure, lower temperature, and a slightly higher catalyst concentration were found to be necessary (29). Plant operations employ 0.3–0.5% catalyst, a temperature of 70–75°C, and a vacuum of 4 kPa or less.

Another variation is the use of triglycerides, such as coconut oil, as the starting material. This involves the reaction of 1 mole of triglycerides with 6 moles of the alkanolamine. The reaction can be catalyzed by sodium methylate at 60°C.

Glycerine is a byproduct that usually remains with the final product. The typical composition of the product consists of 80–85% alkanolamide, 5–7% or less free amine, and traces of fatty acid soap and other byproducts.

The reaction is relatively mild and proceeds readily with the use of 0.2–0.3% sodium methylate catalyst at an operating temperature of 70–75°C and at atmospheric pressure.

9.2. Types of Alkanolamides

There are at least four types of alkanolamide commercially available. The first is formed by reacting monoalkanolamine or dialkanolamine with fatty acids in a 1 : 1 ratio at elevated temperatures of 140–160°C. Significant quantities of the byproducts—amine esters and amide esters—are also formed.

A second major type is the Kritchevsky type made from alkanolamine and fatty acids in the ratio of 2 : 1. Such product contains 60–70% alkanolamide plus byproducts. If diethanolamine is used in addition to the mentioned byproducts, some morpholine and piperazine derivatives are also obtained. The excess alkanolamine renders the product water soluble (29). Both are of commercial importance as detergent and detergent additives.

A third type is the so-called superamide prepared from the methyl esters in a 1 : 1 mole ratio. They are generally products that have an alkanolamide content in excess of 90%. Some of the same byproducts as in the first type are formed but in much smaller quantities. As a result of the relatively small amounts of free alkanolamine, superamides have poor water solubility. They are used in conjunction with a small amount of anionic or nonionic surfactant, which acts as a solubilizer to form a clear viscous solution (29).

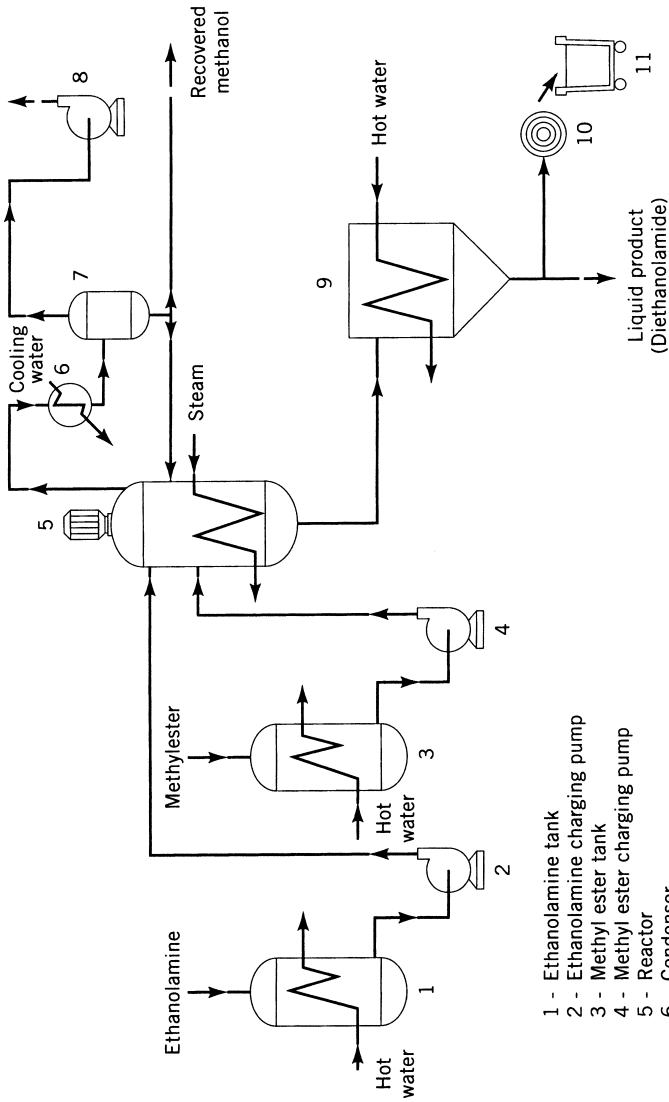
The fourth variant is the product of the direct reaction of a triglyceride with an alkanolamine. The glycerine byproduct is retained with the other byproducts. It is also used as a detergent additive in light-duty liquid detergents.

Other applications of alkanolamides include dry cleaning soaps, fuel oil additives, rust inhibitors, textile scouring, and dye leveling agents.

9.3. Method of Manufacture

Depending on which of the four types of alkanolamide is to be produced, the starting material could be either fatty acid, methyl ester, or triglyceride (coconut oil) and monoethanolamine or diethanolamine. Usually, a batch system of manufacturing is employed, as shown in Figure 20.

Alkanolamide from Coconut Oil. A 2 : 1 cocodiethanolamide (CDEA) can be produced using 6 moles of diethanolamine and 1 mole of refined and bleached coconut oil. The materials are charged with the reactor and a small amount of catalyst (0.25–0.3% sodium methylate or sodium hydroxide) is added. The temperature of the batch is increased to 70–75°C at normal pressure. After 90 min, the reaction is completed. For a 10-t batch, total cycle time from charging the materials, heating them up, allowing the reaction to proceed to completion, and transferring the finished product takes at least 4 h.



- 1 - Ethanalamine tank
- 2 - Ethanalamine charging pump
- 3 - Methyl ester tank
- 4 - Methyl ester charging pump
- 5 - Reactor
- 6 - Condenser
- 7 - Vacuum drum
- 8 - Surge tank
- 9 - Cooled flaking drum
- 10 - Flaked product (monoethanolamide)
- 11 - Liquid product (Diethanolamide)

Figure 20. Manufacture of normal and super alkyloamides (30).

If fatty acid is the starting material, a different operating parameter is used to drive off the water formed during the reaction. If superamide is to be produced, coco-methyl ester and diethanolamine can be used as the starting materials in a mole ratio of 1 : 1. These materials are charged to the reactor with 0.3–0.5% sodium methylate as the catalyst. The reaction is carried at around 100°C and a vacuum of 4–5.3 kPa for a period of 90–120 min. The reaction temperature can be lowered to 70–75°C by employing a vacuum of less than 4 kPa. The reaction time takes longer to enable the maximum vaporization of the methanol byproduct. The methanol is rectified and recycled for use in the transesterification of the coconut oil to produce the methyl ester.

The final product in the liquid form is transferred into the storage tank. Postreaction can be done by keeping the product in another vessel, preferably at slightly elevated temperature for a few days. This allows further conversion of the ester byproduct to amide, thus further increasing the amide concentration.

If monoethanolamine is used as the starting material, the monoethanolamide product (CMEA) is a waxy solid. Accordingly, the finished product after the reaction is passed through a cooled flaking drum to convert it into flakes. It is subsequently packed in bags.

10. SURFACTANTS

Surfactants or surface-active agents make up a special class of chemicals used in practically all industries. Surfactants may be of petrochemical or natural oils origin. This chapter discusses only those of vegetable oil origin, specifically those from coconut oil.

Surfactants are chemical compounds that possess great surface activity. They act so diversely because of the unbalanced molecular structure. A surfactant molecule may be visualized as a tadpole or a mini-racquet. The “head” is the hydrophilic (water-loving), strongly polar portion and the “tail” is the hydrophobic (oil-loving) nonpolar portion. The head can be an anion, a cation, or nonion. The tail is a linear or branched hydrocarbon chain. It is this characteristic configuration that makes surfactants perform such diverse function in industry.

Surfactants find broad application in practically all industries as, for example, the main ingredients of detergents and cleaners, foaming agents and emulsifiers in cosmetics and pharmaceuticals, emulsifiers for paints, scouring agents for textiles, flotation agents for the mining industry, and emulsifiers and sanitizing agents for the food industry.

10.1. Types of Surfactants

Surfactants are classified into four categories: anionic, cationic, nonionic, and amphoteric, each with its own molecular structure and behavior.

Anionic Surfactants. Anionic surfactants are surface-active agents in which the hydrophobic portion is connected to an anion or negatively charged ion. In an

aqueous medium, an anionic surfactant dissociates into a positively charged cation and a negatively charged anion. The latter is the carrier of the surface-active properties. Typical examples are the alcohol sulfates and the ester sulfonates.

Cationic Surfactants. Like the anionic surfactants, cationic surfactants also dissociate in an aqueous medium. However, the head (hydrophilic portion) is a cation, which is the carrier of the surface-active properties. Examples are the quaternary ammonium compounds.

Nonionic Surfactants. The nonionic surfactants do not dissociate in an aqueous medium. Their solubility is provided by the polar group, such as a polyglycol ether or a polyol. The most important types of fatty nonionic surfactants are the polyglycol ethers of fatty alcohols, fatty acids, amines, and amides.

Amphoteric Surfactants. Amphoteric surfactants in aqueous solution contain both positive and negative charges in the same molecule. Thus, a hydrophobic fatty chain is attached to a hydrophilic group that contains both positive and negative charges. Its behavior depends on the condition of the medium or its pH value. Examples of this type are the alkyl betaines.

Coco-Based Surfactants. The most important coconut oil-based surfactants are fatty alcohol sulfate, fatty alcohol ether sulfate, and fatty alcohol polyglycol ether. Two relatively new coco-based surfactants are fatty acid methyl ester sulfonate and alkyl polyglycoside, which is produced from fatty alcohol and starch or sugar, both renewable materials.

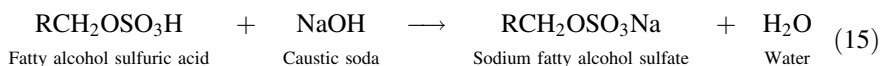
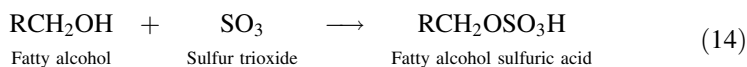
Fatty Alcohol Sulfates. Sodium salt of fatty alcohol sulfate of the C12–C18 range is one of the more common active ingredients of choice in the formulation of laundry detergent products, due to its good detergency, wetting and foaming properties, and biodegradability. The C12–C14 fatty alcohol sulfate, known in the trade as sodium lauryl sulfate (SLS), provides optimum foam and is used extensively as the foaming agent in most toothpastes. The ammonium and alkanolamine salts of the C12–C14 and C12–C16 alcohol sulfates possess high solubility and are well suited for liquid shampoos and bubble bath preparations. In combination with other surfactants and alkanolamides, they deliver desirable qualities, such as fine structured foam, low irritancy, and smooth hair feel (5).

Fatty Alcohol Polyglycol Ethers. The fatty alcohol polyglycol ethers belong to the most important class of nonionic surfactants. They are characterized by having excellent wetting properties, having low foam, and being effective even at low temperatures. They are produced by the reaction of fatty alcohol with ethylene oxide (EO) or propylene oxide (PO), using alkaline catalyst such as sodium methylate or potassium hydroxide. The degree of ethoxylation can vary, depending on the chain length of the fatty alcohol and the purpose for which it will be used. The C12–C14 and C12–C16 alcohols used as raw material for the ether sulfates can have 2–3 moles of EO. The C12–C18 alcohol, with 7–10 moles of EO, are used primarily as wetting agents. Higher saturated alcohols, with up to 30 moles of EO, are used as emulsifiers for waxes and ointments bases. Fatty alcohol polyglycol ethers have replaced the alkylphenol polyglycol ether in most applications. In the United States, however, the latter is still in use for institutional and industrial products because of cost considerations.

Fatty Alcohol Ether Sulfates. Probably the most important derivatives of fatty alcohol in the C12–C14 and C12–C16 ranges are the fatty alcohol ether sulfates. They are produced by the sulfation of the fatty alcohol, containing 2–3 moles of ethylene oxide, with sulfur trioxide or chlorosulfonic acid and subsequently neutralized with caustic soda, ammonia, or an alkanolamine. The ether sulfates possess superior properties over the fatty alcohol sulfates. They have unlimited water solubility, are unaffected by water hardness, and possess superior skin compatibility. Accordingly, they are used in liquid shampoos and bath preparations. One characteristic of this material is its ability to increase its viscosity by the addition of an electrolyte such as salt (5).

10.2. Chemistry of the Reaction

Fatty alcohol sulfate of commerce is actually a neutralized salt primarily as sodium coco fatty alcohol sulfate. It is produced by the direct reaction of fatty alcohol with sulfur trioxide and subsequently neutralized with caustic soda, according to the following reactions:



The intermediate product is a half ester of sulfuric acid. It is quite unstable and must be neutralized immediately. The final product contains approximately 1.5% of sodium sulfate, 1.0–1.5% unreacted alcohol, and less than 0.5% of free alkali.

In sulfation, other sulfating agents may be used, such as oleum or chlorosulfonic acid, as the source of SO_3 . However, oleum generates a large amount of waste sulfuric acid. It is also not recommended for the sulfation of fatty alcohol ethoxylate.

Chlorosulfonic acid is an excellent sulfating agent, but it generates unwanted hydrochloric acid as a byproduct. As a result of the corrosive nature of the hydrochloric acid vapor, special equipment must be used.

In neutralization, other alkali can be used such as ammonia, monoethanolamine, or triethanolamine. The same chemical reaction and equipment applies to the production of fatty alcohol ether sulfate, except that the raw material is fatty alcohol ethoxylate.

10.3. Method of Manufacture

The latest technology in the manufacture of fatty alcohol sulfate or fatty alcohol ether sulfate is the direct use of SO_3 gas as the sulfating agent. This process not only produces a high-purity product but is also much more economical and generates minimum waste.

The heart of the process is the reactor. Reactors can be batch, cascade, or falling-film type. Industry favors the falling-film type because the reaction is much more controllable and highly efficient. Falling-film reactors can be multitube, monotube, or annular (Figure 21).

The manufacture of fatty alcohol sulfate or ether sulfate can be divided into five stages: process air preparation, sulfur trioxide generation, sulfation, neutralization, and exhaust gas treatment.

Process Air Preparation. Process air must be totally dry, preferably with a dew-point below -50°C . The presence of moisture not only makes it corrosive (due to its reaction with SO_3 gas) but also increases the color of the product.

Briefly, air is introduced by a large compressor to a cooling system, where it is cooled down to $3\text{--}5^{\circ}\text{C}$ and most of the moisture is condensed. From there, the air is passed through a dehumidifier, such as silica gel, where the last traces of moisture are retained. Figure 22 shows Ballestra's air drying system.

Sulfur Trioxide Generation. For sulfur trioxide generation, high-purity sulfur (99.5% pure) is melted in a tank and then kept at $145\text{--}150^{\circ}\text{C}$ to maintain its viscosity at the minimum and constant value. The molten sulfur is introduced into the sulfur burner by a special metering pump and then burned to SO_2 , using the dried air. The diluted SO_2 gas (6–7%) leaves the burner at around 650°C and is cooled to 430°C before feeding to the converter.

The catalytic converter, with three to four beds of vanadium pentoxide catalysts, converts SO_2 to SO_3 with up to 98% conversion efficiency. The SO_3 gas is cooled to below 60°C , diluted to 4% by volume, and is passed through a mist eliminator to remove traces of oleum formed before it is fed to the reactor. Figure 23 shows a typical system for the generation of SO_3 gas.

Sulfation. The sulfation is carried out in a multitude film reactor, especially designed to control accurately the mole ratios between the SO_3 and the organic feed in each tube. The materials enter the top section and flow cocurrently downward inside the tube. As the reaction is almost instantaneous and exothermic, cooling water at controlled flow is introduced into the jacket to maintain the reaction temperature at $45\text{--}50^{\circ}\text{C}$ maximum. A reaction yield of 97% can easily be achieved (see Figure 21).

Neutralization. The intermediate product from the reactor must be neutralized immediately, as hydrolysis may occur and badly affect the process and the product quality. This is achieved in a double-step continuous neutralization unit. The multi-bladed mixer gives exceptionally homogeneous mixing (30).

It is important that the neutralized paste be kept slightly alkaline to ensure processability and product stability. An average concentration of 72% active matter is readily achievable. A much higher concentration is not recommended, as processing difficulties may be encountered. If a dried product is desired, the paste can be further processed through a wiped film evaporator. Figure 24 shows Ballestra's double-step neutralization.

Exhaust Gas Treatment. The gas effluent must be treated to comply with environmental regulations. The exhaust gas from the reactor contains traces of organic matter and unreacted SO_3 and SO_2 gases. The first two impurities are removed by

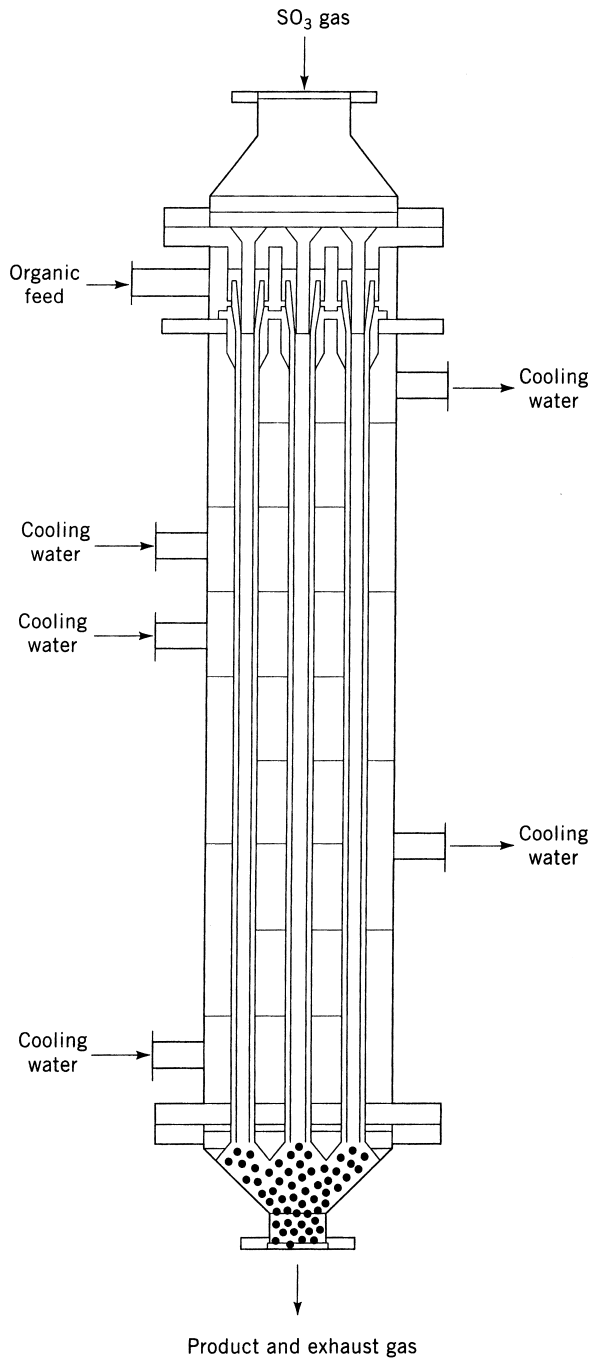


Figure 21. Multitube film reactor (30).

- 1 - Process air filter
- 2 - Process air compressor
- 3 - Chiller
- 4 - Air cooling group
- 5 - Circulating pump
- 6 - Glycol recycle vessel
- 7 - Circulating pump
- 8 - Silicagel regeneration unit
- 9 - Regeneration air fan
- 10 - Silicagel air dehumidifier

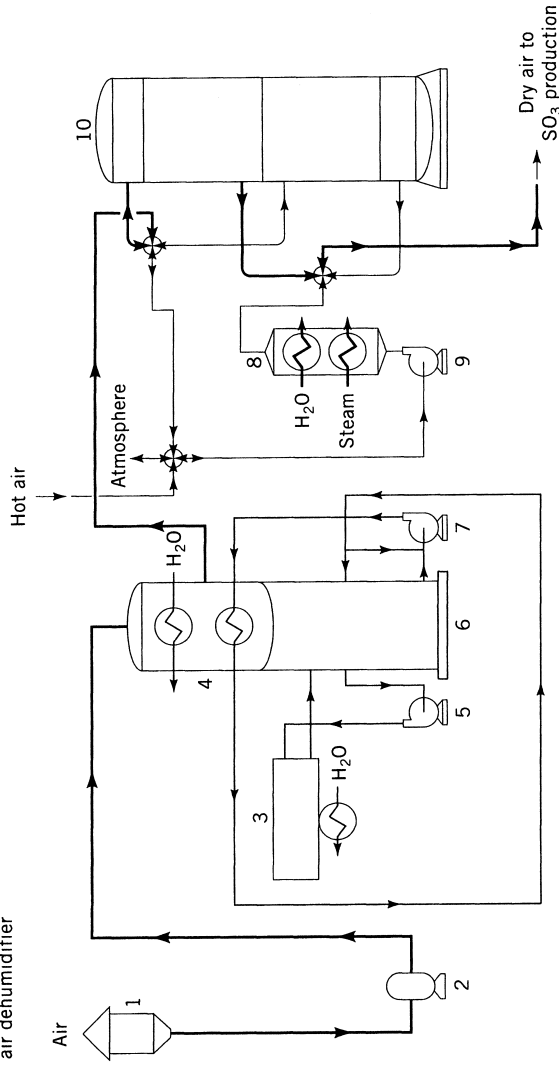


Figure 22. Ballestra's air drying system (30).

- 1 - Sulfur melting vessel
- 2 - Molten sulfur filter
- 3 - Molten sulfur dosing unit
- 4 - Sulfur combustion furnace
- 5 - Preheating air generator
- 6 - SO₂ cooler-preheater
- 7 - Catalysis tower
- 8 - Interstage heat exchangers
- 9 - Electric igniter
- 10 - SO₃ coolers
- 11 - Cooling fan

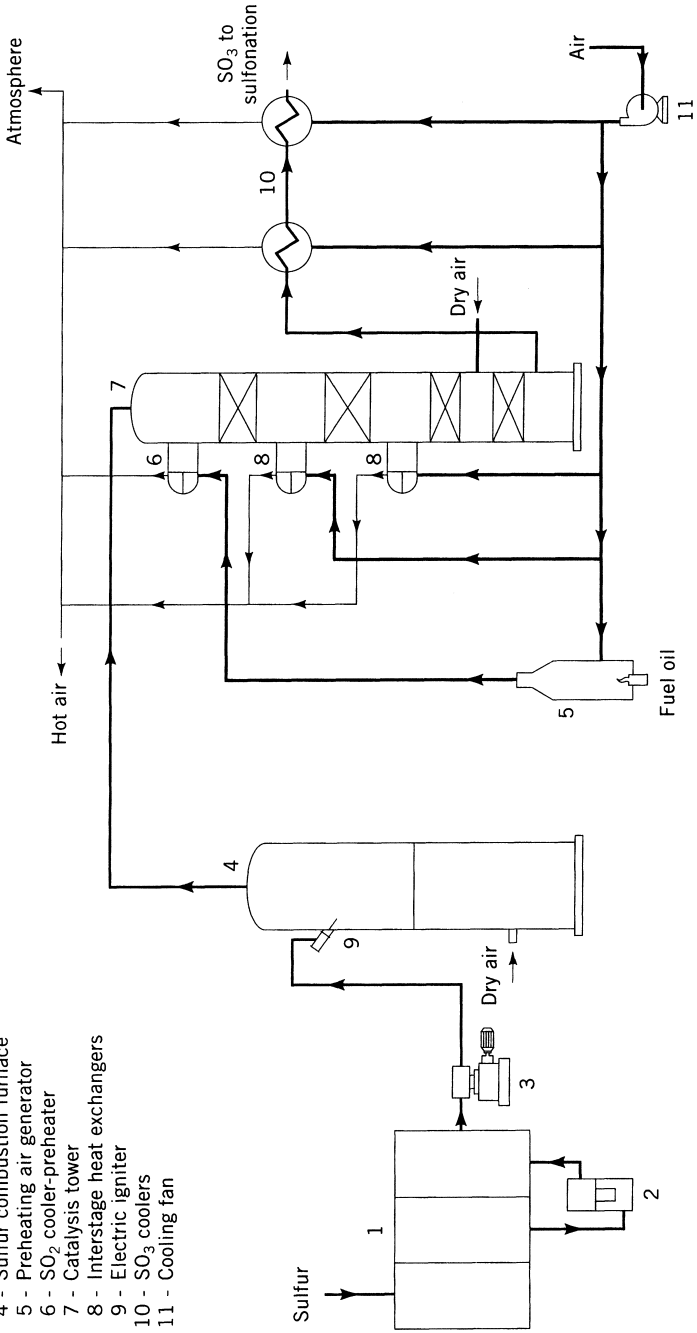


Figure 23. Ballestra's SO₂-SO₃ production (30).

- 1 - Water dosing unit
- 2 - Caustic soda dosing unit
- 3 - 1st Neutralizing reactor
- 4 - Recycle and transfer pump
- 5 - Neutralization heat exchanger
- 6 - 2nd Neutralizing reactor
- 7 - pH Control unit
- 8 - Final homogenizing unit
- 9 - Active matter transfer pump

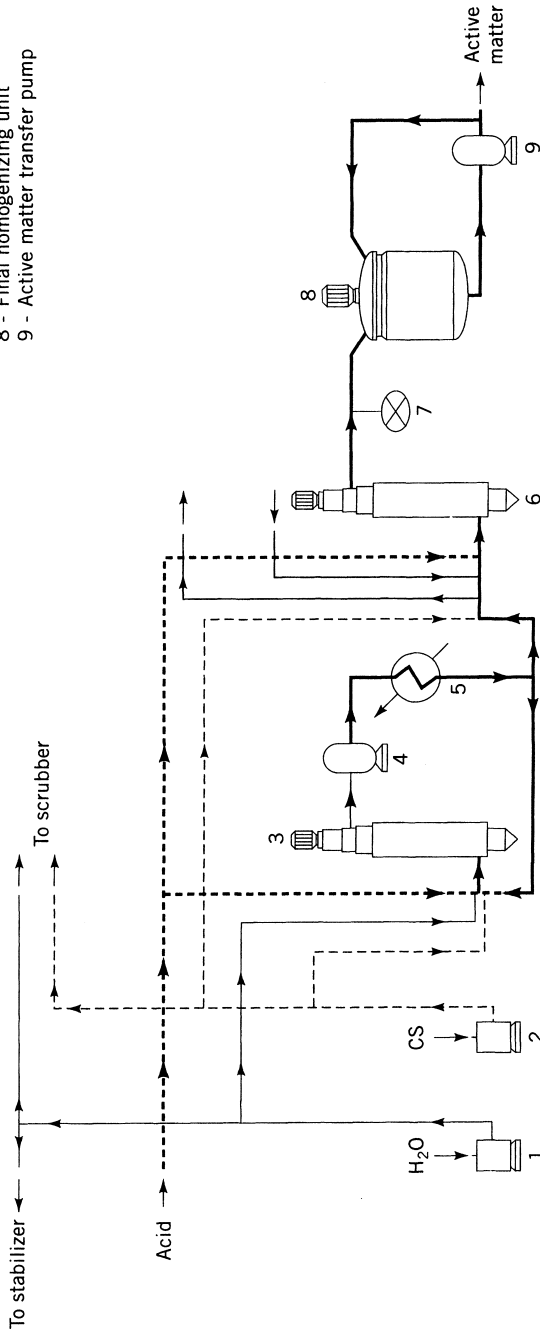
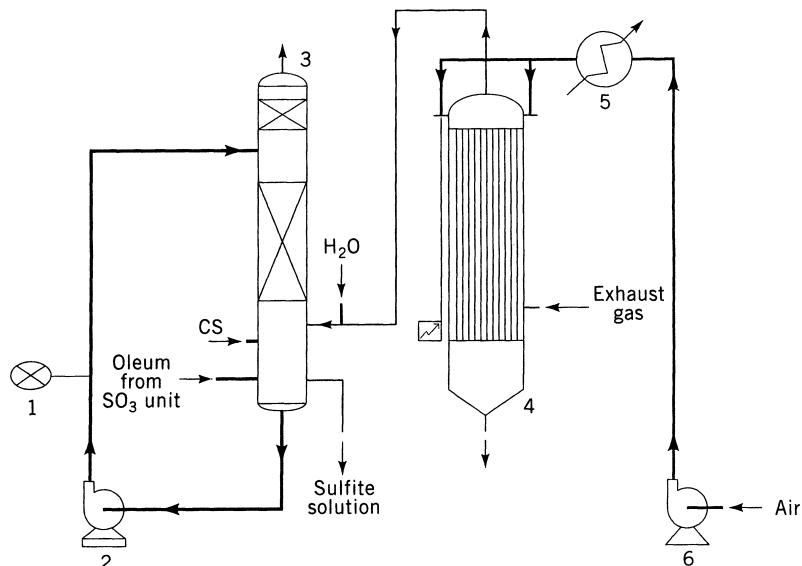


Figure 24. Ballestra's double-step neutralization (30).



- 1 - pH Control unit
- 2 - Scrubbing solution circulation pump
- 3 - Gas scrubbing column
- 4 - Electrostatic precipitator
- 5 - Air heater
- 6 - Air fan

Figure 25. Ballestra's gas-scrubbing system (30).

the electrostatic precipitator. The remaining SO_2 gas is removed by the reaction with caustic soda solution flowing countercurrently inside the scrubbing column. The concentration of the residual SO_2 in the exhaust gas vented into atmosphere is kept at 5 ppm maximum, well below the allowable standards (Figure 25).

10.4. Sulfonation of Fatty Acid Methyl Esters

Fatty acid methyl esters sulfonate may be considered a material with a great potential. Its superior sequestering effect on water hardness gives it an advantage over fatty alcohol sulfate. The sulfonation of fatty acid methyl ester is different from that of fatty alcohol. The reaction mechanism involves two steps (31). In the first reaction, the SO_3 gas reacts quickly to form sulfoanhydride. In the second step (which takes 40–90 min), the sulfoanhydride becomes the sulfonating agent, reacting with the still-unreacted ester.

The reaction requires an excess of SO_3 in the range of 20–30 mol % to get initiated. With such an excess, the formation of disalt during neutralization is unavoidable. This is somehow minimized by subsequent re-esterification after the second step.

The neutralization step can be carried out in much the same way as in the neutralization step in the production of fatty alcohol sulfate. As a result of the nature of the reaction and conditions during sulfonation, a dark-colored product is produced, which requires bleaching. Postreaction treatment with H_2O_2 and NaOCl yields a product with an acceptable color (30).

10.5. Other Surfactants

Three highly successful types of coco-based surfactants used in toilet soap formulations that are mass marketed in the United States are worth mentioning. They impart superior hardwater lather performance while retaining the mildness aspect of toilet soap. These are (1) sodium cocoyl isethionate (SCI) used in Lever's Dove and their other brands, (2) sodium cocoglyceryl ether sulfate (LGES) used in Procter & Gamble's Zest, and (3) sodium cocomonoglycerides sulfate (CMGS) used in Colgate's Vel Bar (4).

Other coco-based surfactants are sulfosuccinates formed by the reaction of coco fatty alcohol with maleic anhydride and further reaction with sodium sulfite or bisulfite. This product possesses good foaming properties, is compatible with soap, and is a good lime dispersant. It is used in toilet soap formulation, shampoos, hand cleaning pastes, and for scouring raw wool. Its ether variant, with 2–4 moles ethylene oxide, forms intense, finely structured foam and is used in combination with ether sulfate in baby shampoos and bath preparations.

Alkyl phosphates, also coco based, are formed by the reaction of fatty alcohol with phosphorous pentoxide. The product is a mixture of monoesters and diesters. Its sodium salt (MAP) is reportedly mild and is used in facial wash, such as Kao's Biore. Other uses are as antistatics in textile auxiliaries, corrosion inhibitors, surfactant additives for extreme pressure (EP) lubricants, and surfactant components in alkali and acid cleaners. Coco-based alkyl polyglycosides (APG) have been successfully produced and marketed by Henkel in the United States. The alkyl polyglycoside fully satisfies the demand for a mild surfactant and is completely biodegradable.

11. TERTIARY AMINES

Fatty amines and their derivatives represent the most important nitrogen compounds of fatty acids. They possess great ionization constants compared with other alkyl derivatives of ammonia. They are cationic, basic, biologically active, and strongly adsorbed on many surfaces due to their high adsorption potential. They are indispensable in many surface-related physicochemical processes. They are the starting materials for the manufacture of quaternary ammonium compounds and various cationic and amphoteric substances. These derivatives find wide application in many industries as biocides, sanitizing agents for algae control in water treatment, ore flotation agents in mining, effective corrosion inhibitors, and lubricants in drilling and formulation. Fatty amines derived from tallow or palm oil fatty acid fractions are widely used in the production of fabric softeners.

The main raw material is the fatty nitrile derived from the reaction of fatty acid with ammonia. Catalytic hydrogenation of the nitrile produces the amines. The amines are available as primary, secondary, and tertiary amine, depending on the number of the alkyl groups attached to the nitrogen atom.

11.1. Types of Tertiary Amines

Of the three fatty amines, the tertiary fatty amines, with three alkyl groups, find the most application in industries. They are further classified into three types: (1) symmetrical trifatty amine (R_3N), in which all three alkyl chains are identical; (2) asymmetrical dimethyl fatty amine $[RN(CH_3)_2]$ or methyl difatty amine (R_2NCH_3); and (3) those derived from primary or secondary amine by the reaction with ethylene oxide. These asymmetrical fatty amines are the bases for the manufacture of organomodified clay for the petroleum industry, biocides, and algicides.

11.2. Methods of Preparation

Several methods are available for the preparation of tertiary amines from fatty acids. One of the oldest is the classical Leuckart reaction (32), which uses formaldehyde and formic acid for the reductive alkylation of a secondary amine.

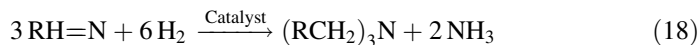


Modification to this reaction had been reported. Shapiro (33) developed the reductive alkylation of primary and secondary amine with formaldehyde in the presence of nickel catalyst.

Of commercial importance is the manufacture of fatty amines via the nitrile route. Fatty acid is first converted to nitrile by the reaction with ammonia at elevated temperatures of 280–360°C at atmospheric pressure.



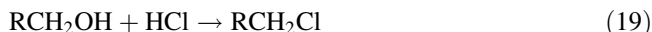
The reaction that produces the nitrile is essentially a dehydration reaction of the intermediate product. The nitrile is then catalytically hydrogenated to produce the fatty amines.



Depending on the process conditions, primary, secondary, or tertiary amines can be produced. If more tertiary amines are desired, continuous removal of the NH_3 is necessary to shift the reaction forward. The presence of ammonia favors the formation of primary and secondary amines.

Fatty alcohols are also available raw materials in the commercial preparation of tertiary amines. The fatty alcohol may be converted directly to an alkyl halide by

the reaction with a concentrated hydrogen halide (5). The alkyl halide can then be reacted with dimethylamine to produce the tertiary amine (33).



Long-chain alcohols can be converted directly to *N,N*-dimethylalkylamines by the reaction with dimethylamine at 36°C in the presence of $\text{Th}(\text{SO}_4)_2$ or in the presence of Cu–Cr catalyst and hydrogen at elevated temperatures and pressure (33, 34).



Ethoxylated tertiary amines can be produced by the reaction of primary or secondary amines with ethylene oxide. The water solubility of this amine increases with the increasing degree of ethoxylation (33).

11.3. Uses

The asymmetrical tertiary amines are used exclusively as starting materials for the manufacture of quaternary ammonium compounds, cationic and amphoteric surfactants, and amine oxides. Quaternary ammonium compounds used as bactericides and algicides are produced by the reaction of tertiary amines with benzyl chloride, methyl chloride, or dimethyl sulfate. Of these, the benzyl ammonium chloride salt is the most widely used.

Probably the largest volume use of fatty amines is in the manufacture of fabric softeners. The latter is distearyldimethyl ammonium chloride produced by the reaction of distearylamine and methylchloride with continuous addition of alkali. However, as stated earlier, the starting materials for this product are the C16–C18 fatty acid fractions from tallow or palm oil.

Tertiary amines are also used in the manufacture of amine oxides by the oxidation with hydrogen peroxide. The amine oxides are used in cosmetic preparations for its good foaming properties and mildness to the skin. Another raw material used in the cosmetic industry is the betaines produced by the reaction of a tertiary fatty amine with sodium chloroacetate. The betaines exhibit good foam stability over a wide range of pH, are insensitive to water hardness, and are mild to the skin (33).

REFERENCES

1. S. Marash, R. Gubler, and K. Yagi, "Fats and Oils Industry Overview," *Chemical Economics Handbook*, SRI, Menlo Park, California, 2001.
2. R. Modler, R. Gubler, and K. Yagi, "Natural Fatty Acids," *Chemical Economics Handbook*, SRI, Menlo Park, California, 2002.

3. "Alcohols, Higher Aliphatic Synthetic Processes," in *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 2, 5th ed., Wiley-Interscience, Hoboken, New Jersey, 2004, p. 28.
4. L. Spitz, *Soap Technology for the 1990's*, AOCS, Champaign, Illinois, 1990.
5. H. Schutt, H. D. Kamp, H. P. Kubersky, and J. Glasl, *Fatty Alcohols*, Henkel KGaA, Dusseldorf, 1982.
6. B. Brackman, J. Knaut, and P. Wallscheid, *Oleochemicals*, Henkel KGaA, Dusseldorf, 1984.
7. *Fatty Acid, Product Specifications 1993*, United Coconut Chemicals, Inc., Metro Manila, Philippines, 1993.
8. H. J. Richtler, *Challenges to a Mature Industry*, Henkel KGaA, Dusseldorf, 1983.
9. U.S. Patent 601,603, 1897.
10. D. Swern, ed., *Bailey's Industrial Oil and Fat Products*, vol. 2, 4th ed., John Wiley & Sons, Inc., New York, 1982, p. 107.
11. *Fatty Acid Technology*, Technical brochure no. 197e/3.91/30, Lurgi AG, Frankfurt, 1991.
12. W. M. Linfield, R. A. Barauskas, L. Sivieri, S. Serota, and R. W. Stevenson Jr., *J. Amer. Oil Chem. Soc.*, **61**(2), 191–195 (1984).
13. *Advanced Technology and Services for Oleochemical and Tall Oil Processing*, Technical brochure Badger, Cambridge, 1990.
14. B. Freedman, *Methyl Ester—Manufacture and Utilization*, U.S. Department of Agriculture, Peoria, Illinois, .
15. U. R. Kreutzer, *J. Amer. Oil Chem. Soc.*, **61**(2), 343–348 (1984).
16. T. Ogoshi and Y. Miyawaki, *J. Amer. Oil Chem. Soc.*, **62**(2), 331–335 (1985).
17. T. Voeste and H. Buchold, *J. Amer. Oil Chem. Soc.*, **61**(2), 350–352 (1984).
18. *Fatty Alcohol Process*, Technical brochure no. 1480 e/2.91/2.7, Lurgi AG, Frankfurt, 1991.
19. F. de Dardel, *Glycerine Purification*, Rohm & Haas, Paris, 1989.
20. D. H. Chadwick and R. S. Watt, *Phosphorus and Its Compounds*, vol. 11, Interscience Publishers, New York, 1961.
21. M. Dahanayake and W. Kristoff, *Phosphate Ester Hydrotropes*, HAPPI, Ramsey, New Jersey, 1992.
22. H. Adler and W. H. Woodstock, *Chem. Ind.*, **51**, 516 (1942).
23. J. M. H. Daemer and W. Dalkelman, *J. Chromatogr.*, **78**, 281–291 (1973).
24. W. Kritchevsky, U.S. Patent 2,089,212, August 10, 1937.
25. W. Kritchevsky, U.S. Patent 2,096,749, October 26, 1937.
26. E. Meade (to Lankro Chemicals, Ltd.), U.S. Patent 2,464,094, March 8, 1949.
27. G. Tesoro (to Onyx Oil and Chemical Co.), U.S. Patent 2,844,609, July 22, 1958.
28. J. Schurman (to Colgate Palmolive Co.), U.S. Patent 2,863,888, December 9, 1958.
29. *Alkanolamines handbook no. 111-1159-88 R*, SAI, Dow Chemical Co., Midland, Michigan, 1988.

30. A. Davidsohn and G. Moretti, paper presented at the International Symposium on Natural Base Cleaning Agents and Personal Care Products, Marseille, 1985.
31. A. J. Stirton, *J. Amer. Oil Chem. Soc.*, **39**, 490 (1962).
32. H. Maag, *J. Amer. Oil Chem. Soc.*, **61**(2), 259–267 (1984).
33. S. H. Shapiro, *Fatty Acids and Their Industrial Applications*, Marcel Dekker, Inc., New York, 1968, pp. 123–128.
34. S. Billenstein and G. Blaschke, paper presented at the World Conference on Oleochemicals, 1984.