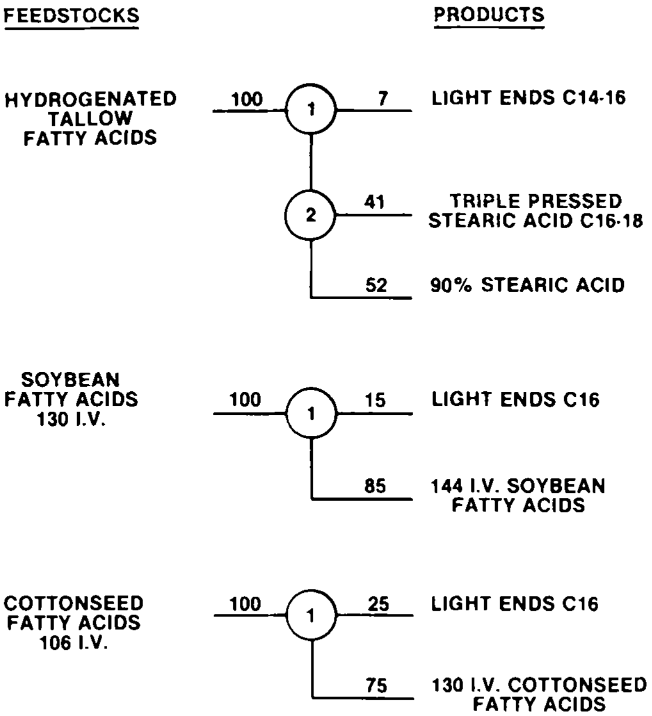

FIG. 4. Partial fractionations.

to fractionate fatty acids. Distilled fatty acids, however, can be put through this unit a second time, and by adjusting reflux ratios and temperatures separate high and low boiling fractions can be obtained with the low boilers collected in the product section and the high boilers brought out the residue section.

Because all fractionating trays have a pressure drop of from 1–2 mm, and fatty acids are heat sensitive, fractionating stills are limited to ca. 20–30 trays, depending on the vapor pressure of the fatty acids to be separated. Any more trays would cause pressure in the reboiler section to be higher than 30–50 mm. The vaporization temperature at higher absolute pressures may exceed the decomposition temperatures of the fatty acids. Because of this limitation to get high purity fatty acids from two to six fractionating stills may have to be used for continuous operation.

Figure 3 shows a fractionation system for crude or distilled fatty acid feedstocks. The low boiling fraction is condensed off the top of the first still, and the high boiling fraction from the bottom of the fractionation still is sent to a second stripping still. The high boiling product is distilled and condensed off the top of the second still.

Nonvolatile impurities originating in the crude feedstock or traces of nickel catalyst from hydrogenated feedstocks, along with polymerized materials formed in the fractionating still, are taken out the bottom as residue.

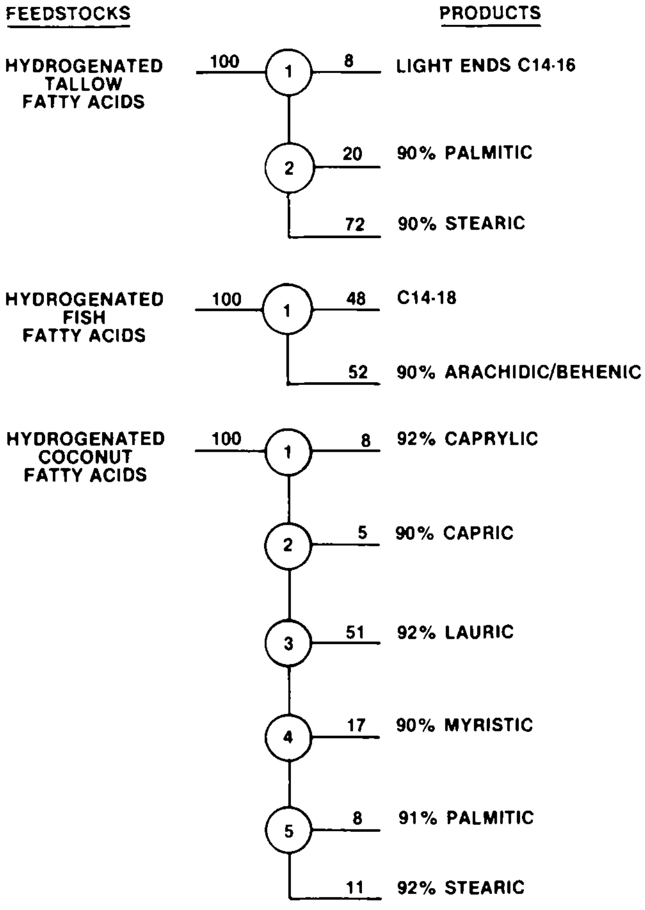

FIG. 5. Full fractionations.

Fractionation stills are almost always custom designed to suit available feedstocks and product requirements. With lauric type fatty acids from coconut or palm kernel oils, up to 30 trays can be used for highest purity fractions because of the higher volatility and greater stability of the short chain saturated acids. Long chain fatty acids from fish oils and high erucic content rapeseed oil have much lower vapor pressures and would need low pressure drop packing or a limited number of fractionating trays to keep the reboiler below the decomposition temperature.

Molecular stills or thin film stills are used for simple distillation of heat sensitive products of low volatility but cannot perform clean separations that require more than one equilibrium stage.

Figures 4 and 5 show commercial products that can be obtained from fractional distillation stills.

Interrelationships in Fatty Acid Processing

E. FRITZ, Process Development, Union Camp Chemical Div.,
PO Box 570, Savannah, GA 31402

ABSTRACT

Examples are presented of the effect of each processing step on the quality, yield and throughput in the fatty acid processing scheme. These examples serve to illustrate the importance of seemingly unimportant process variables upon the economics involved in fatty acid processing.

Fatty acids are seldom sold or used as a crude product. They are more frequently processed through a series of unit operations and processes. These are depicted in Figure 1. As in most series of processes, the operation of each has an effect upon subsequent ones.

Most of our raw materials are byproducts of other industries and as such, are generally variable in quality. For example, tallows and greases are byproducts of the meat industry. However, depending upon rendering techniques used, there will be varying amounts of proteinaceous materials, color, free fatty acid, moisture and unsaponifiable material. Bleachable tallow, for example, can be purchased at a 9 FAC color and at a 23 FAC color and still be considered bleachable tallow according to the trading rules. Because of the variable nature of the raw materials, some sources, especially those containing high percentages of proteinaceous material, can lead to problems in the fat splitting process if the high pressure continuous splitter is used. Some of these problems are emulsions in the fat splitting tower, low conversion of fat to fatty acids, high fat in sweetwater, and subsequent low yields upon distillation caused by reversion of mono- and diglycerides to triglycerides. All of these glycerides are nondistillable in conventional distillation equipment and end up downgraded to pitch.

With the addition of city fat pickups, the fats from butcher shops, meat processing plants and fast-food chains, we find another very insidious contaminant – polyethylene. You are all familiar with the usual form of polyethylene; we pack shortening, meat scraps, and fats from meat processing plants in polyethylene bags. However, when the bag is rendered along with the fat and is subsequently fed to the fat splitter, it looks like a fused, black, plastic mass. This plastic material adheres to the walls, internals, sparge ring, and water distributor of the fat splitter, causing channeling of the water through the fat layer and allowing free glycerine to go out with the fatty acids. This, then, causes reversion of the fatty acids back to the glycerides and again adversely affects the yield and quality of the finished fatty acids. Renderers could filter the tallows and greases at 75-80 C to remove the majority of the polyethylene. It is best to check incoming feeds so that preventive measures can be taken, because the best method of practically and adequately removing this mass is to shut down and scrape the system free of polyethylene. This is very costly.

Continuing to the next step in the sequence of the fat splitting operation, feed quality becomes an important consideration, and some thought should be given to pretreatment. This may, for example, be as simple as settling or require water washing and/or filtration, or more involved techniques. Using the continuous splitter, it is possible to achieve splits in excess of 98%. It is important, however, to note that any free hydroxyl group left as the monoglycerides or diglycerides or as free glycerine, will tie up a molecule of fatty acid and reduce the yield of distilled fatty acid. For example 0.1% free glycerine will tie up ca. 1.0% of fatty acids as the triglyceride.

Temperatures employed during the splitter operation also have an important effect upon quality and yield. Highly unsaturated fats, like those from linseed and fish oils, can polymerize to products which are nondistillable in conventional fatty acid stills. Use of too much internal steam can cause emulsions and carryover of glycerine in the fatty acid system.

The use of catalysts to increase the capacity of continuous fat splitters has been demonstrated. Zinc oxide has been commonly used at levels up to 0.5% of the fat feed. Using catalysts like zinc, however, usually results in a compromise. One must determine where the zinc ends up and what we do with the zinc soaps. Our experience has been that zinc usually ends up in the distillation pitch, results in a loss of fatty acid yield, requires acidulation to recover fatty acid, and may, subsequently, result in water pollution problems. The use of catalysts, however, is usually dictated by the economics of a particular business situation.

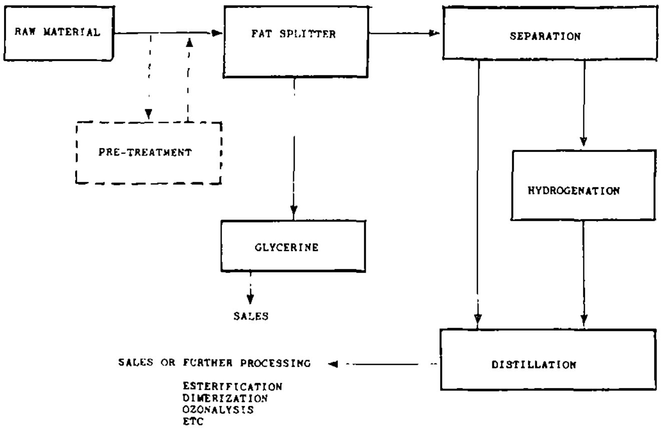

FIG. 1. Fatty acid processing.

Sweetwater from continuous high pressure splitting is greatly affected by the quality of the water fed to the system. Raw water containing high levels of minerals, such as calcium, not only causes loss of fatty acid yield with the formation of calcium soaps, but in addition, these soap scums can cause filtration problems, and if deionization is used, may cause fouling of the deionization beds and require more frequent regeneration of these beds. This more frequent regeneration is a cause of low glycerine yields and high BOD in the waste water. One further note on glycerine processing: it is important that the equipment, including sweetwater storage, be kept clean and free of bacteria. Bacterial contamination can cause high glycerine losses in storage, and this situation is difficult to detect because many plants inventory glycerine content of sweetwater by analyzing a monthly composite. The losses show up as low monthly production yields. This can be overcome by storing the sweetwater at temperatures above 70 C.

The next step in the processing of tallow fatty acid, is solid-liquid separation. Technological advances in recent years have all but eliminated the traditional pressing methods of separating solid from liquid fatty acids. Most of the processes in use today are either solvent separation, using either methanol or acetone, or the aqueous system, utilizing detergent wetting techniques. Each process has its strengths and weaknesses. While solvent systems give good separations and quality of both products, they are energy intensive and are potential sources of air and water pollution. Glycerides in the feed to solvent systems can cause problems with filtration which can result in partial blinding of the cloth, reduced filtration rates, difficulty in cake washing and poor product quality. The first installations of the aqueous system had some difficulties in obtaining a 0 to 5° titer oleic and a stearic acid with an iodine value under 15. This high iodine value stearic, when hydrogenated, produced a noneutectic stearic acid and did not have the same crystallization properties as a eutectic stearic containing ca. 55% palmitic to 45% stearic acid. This early shortcoming of the aqueous process has reportedly been improved in later installations and now is capable of producing good quality oleic and stearic acids.

Continuing in the processing sequence to the hydrogenation of fatty acids, many processing problems encountered can frequently be traced to a raw material source. One of the most common problems found is poisoning of the nickel catalyst with residual soaps and sulfur compounds found in feedstocks. Pretreatment of the fatty acids with spent nickel catalyst, or bleaching with clays, are frequently used as means of removing or reducing the effect of these poisons.

Besides being a hydrogenation catalyst, nickel also is an oxidation catalyst being more effective in concentrations of only a few ppm. Nickel reacts with fatty acid during hydrogenation, forming soluble nickel salts which serve as an oxidation catalyst, especially when heated to a high temperature in the presence of air. Therefore, if you think you have removed all of the nickel by filtration, you are probably wrong. Some plants remove traces of nickel by using sequestering agents such as citric acid or phosphoric acid. Incomplete removal of nickel after hydrogenation has an adverse effect upon color stability of distilled fatty acids.

Trans-isomer formation during splitting and during selective hydrogenation produces elaidic acid from the oleic acid. Elaidic acid has a high titer and can result in the production of high iodine value stearic acid or high titer oleic acid.

Exposure of unsaturated fatty acids to air at elevated temperatures can cause color and color stability problems and odor stability problems by the formation of peroxides. Therefore, it is important to have a good deairator in the feed line to the distillation tower. Traces of air in steam sparging during distillation has the same adverse effect. It is also very important to protect the finished distilled fatty acids in storage by blanketing the tanks with inert gas in order to exclude air. Overheating unsaturated fatty acid can produce thermal dimer formation, and these higher molecular weight acids end up in pitch.

Unremoved bleaching clays in products that are subject to later high temperature operations may cause trans-isomer formation. An operator knowing that an oleic acid contains clay after having been clay bleached and filtered, and knowing that the product has to be distilled and the clay will be removed in the residue cut, may decide to distill the oleic acid containing clay. The finished oleic acid meets all specifications except for titer. What happened? Oleic acid (*cis*-9-octadecenoic acid) that has been clay bleached but given a poor filtration can be catalytically converted to elaidic acid (*trans*-9-octadecenoic acid). Since elaidic acid has a higher melting point than oleic, the resulting product had a higher than normal titer.

Formation of "positional" isomers during selective hydrogenation gives an oleic acid that produces by ozonolysis an azelaic acid that is of altered composition and of radically different polymer properties. Consider, if you will, that you are given the job of improving the process to produce azelaic acid and pelargonic acid by ozonolysis of oleic acid. Commercial oleic acid, as you know, contains 5-10% linoleic acid (*cis,cis*,9,12-octadecenoic acid). Linoleic acid when subjected to ozonolysis will give azelaic acid and caproic acid and uses 2 moles of ozone per mole of linoleic acid. This is twice the amount of ozone it takes to cleave oleic acid which has only one double bond. This is a waste of ozone. Therefore, you decide to remove this polyunsaturated material by selective hydrogenation. The hydrogenated product contains only traces of polyunsaturates, and only a slight increase in saturates was observed. The product upon ozonolysis gave not only azelaic acid, but also many other dibasic acids. These mixed dibasic acids gave a polymer with radically different properties, as expected, than one from "pure" azelaic acid. What happened? The problem lies in the hydrogenation step. Hydrogenation catalysts are also isomerization catalysts causing shifts in the double bond up and down the chain. Thus, after a partial hydrogenation, the *cis*-9-octadecenoic acid is converted into *cis* and *trans* positional isomers from near the carboxyl group all the way out to near the end of the chain.

Loss of polyunsaturates during certain splitting operations affords a high linoleic acid that polymerizes slower and yields a dimer acid of a different structure. In order to thermally dimerize a fatty acid, that fatty acid must be polyunsaturated. Commercial fatty acids fitting this description are soybean, linseed, fish and tall oil. Soybean oil, for example, contains 5-11% linolenic acid which polymerizes at a faster rate than either oleic or linoleic acids. When some of this linolenic acid is removed as polymer during splitting, it then causes the resulting fatty acid to polymerize at a slower rate and to give a dimer with somewhat less dicyclic unsaturated structure.

Up to now, we have concentrated on animal and vegetable fat. However, another very important feedstock for the fatty acid industry is tall oil. Tall oil is also a byproduct and varies in quality as do the animal and vegetable fatty acids. Crude tall oil, for example, varies in acid number from 120 to 180, depending upon the source of wood, climatic conditions during growth, and processing conditions during acidulation. The yield of finished fatty acids and rosin acids is directly related to the acid number of the feed. The lower acid number indicates a higher percentage of neutrals, most of which are nondistillable. High solids caused by high residual black liquor from the sulfate paper-making process result in fouling of heat exchangers with sodium sulfate and lignin during distillation. Some processors use a soap-washing process to reduce the concentration of black liquor to improve the quality of the crude tall oil. The use of spent acids containing chlorides used in the paper-bleaching process may cause severe corrosive conditions unless steps are taken to insure low residual chloride content of the crude tall oil.

Just a few words about materials of construction for fatty acid processing. The use of aluminum is acceptable for fatty acid storage and transfer lines. However, it is important that water and caustic cleaners be kept out of the system because each can cause severe corrosion. While 304 stainless steel is acceptable for storage of the fatty acids, it is recommended that 316 stainless steel be used for the heating coils and agitator as these are subject to higher rates of corrosion caused by high temperatures and velocity effects. Higher temperatures used in processing, especially in distillation, may require the use of higher alloy steels. Short chain fatty acid, in particular, at these higher temperatures, may require steels with higher molybdenum contents. This is especially true in distilling tall oil fatty acids.

One additional point: be sure that there are no copper or brass valves, inserts, bushings or other equipment in contact with fatty acids. Trace amounts of these salts result in a green cast to the fatty acids and color instability problems. Also, even though carbon steel may be used to store fatty acids at a low temperature and not corrode the equipment, trace amounts of iron soaps also cause color stability problems.