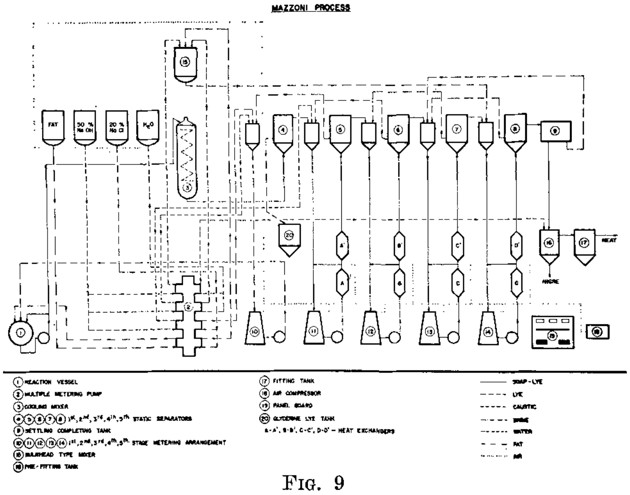

FIG. 9

3. Finally, with glycerine prices declining you should examine the cost of putting on wash lyes. It is feasible to completely eliminate the wash lyes and the half finish without changing the glycerine recovery greatly.

If new production facilities are needed, then consideration should be given to installing one of the *continuous* saponification processes. They require about one-tenth the usual kettle house space for equal production. They require a little more electricity for pumps and mixers, but save a great deal of steam. All of them are producing acceptable soap in some part of the world. The De Laval process is probably the best from the point of view of ease of getting on stream and adjusting to variations in composition of fat stocks, but it is the most expensive and, as presented here, is more costly than the others to operate because of the excess caustic in the glycerine lyes. With all the continuous processes you may find a difference in the odor of the soap produced because of the lack of steam distillation during processing and either the separation of no niger or recycling without taking off a niger degrading.

REFERENCES

1. Bailey—Industrial Oil & Fat Products, 2nd edition, p. 844.
2. Ferguson, R. H., Oil & Soap, *14*, 115–118 (1937).
3. Davidsohn, Better, and Davidsohn, Soap Manufacture, Vol. 1, p. 82.
4. Jones, L. D., JAOCS, *35*, 630 (1958).

# Manufacture of Soap from Fatty Acids

**A. B. HERRICK and ERIC JUNGERMANN, Soap Research and Development Dept.,**
**Armour & Company, Chicago, Illinois**

SOAP MANUFACTURE via the fatty acid route has been practical only since the development of continuous fat-splitting equipment of the countercurrent type in the 1930's and 1940's by workers at Colgate-Palmolive-Peet Company, Emery Industries, and Procter and Gamble (1,2,3).

The two general methods of making soap, 1) direct saponification of fat and 2) fat splitting followed by distillation and saponification, both have some advantages and disadvantages. The many features of direct saponification of triglycerides by batch and continuous methods are covered by another paper (4) presented at this Short Course.

It is the purpose of this paper to describe the processes and equipment involved in manufacturing soap from fats via fatty acids in some detail, and to discuss the advantages and disadvantages of the various soap making procedures. A simplified schematic diagram of the process being described is shown in Figure 1.

### Fat Splitting

A number of excellent reviews have been written on fat splitting (5,6,7) and fatty acid distillation. Essentially, the hydrolysis of triglycerides to fatty acids and glycerine by reaction of water and fat under conditions of high temperature and pressure is a simple chemical process. To obtain high yields of fatty acids, the reverse reaction in the equilibrium must be repressed by countercurrent washing to remove the glycerine from the reaction zone. A simple diagram of a fat splitter is shown in Figure 2. The rate of the reaction is controlled by the temperature in the splitter and by the amount of catalyst used.

An important feature in the design of the fat splitter and auxiliary equipment is whether a catalyst is to be used or not. The catalyst most often employed in commercial splitters is zinc oxide. Others tried include NaOH, KOH, LiOH, MgO,Ca($OH_2$). The zinc catalyst is converted to zinc soaps before the fat enters the splitter. This catalyst was found by Lascaray (8) and was the most effective one tried. The function of this catalyst is to assist in emulsifying the triglyceride oil with water to permit the hydrolysis to begin without the lengthy induction period otherwise required. When a certain amount of hydrolysis to fatty acid has occurred, the solubility is greatly increased and the reaction proceeds rapidly.

If a catalyst is employed, additional equipment is required to mix the zinc oxide with the fat and get it into solution before the fat enters the splitter, and also to remove it from still bottoms after distillation.

Without a catalyst, a larger splitter is required to obtain the same rate of throughput at the equivalent extent of reaction (97–99% split). Since other aux-

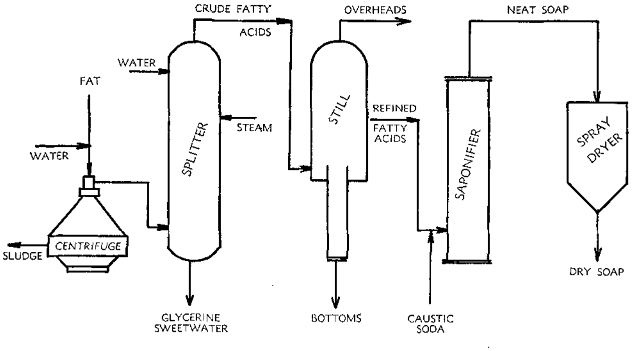

FIG. 1. Schematic diagram of fatty acid route to soap.

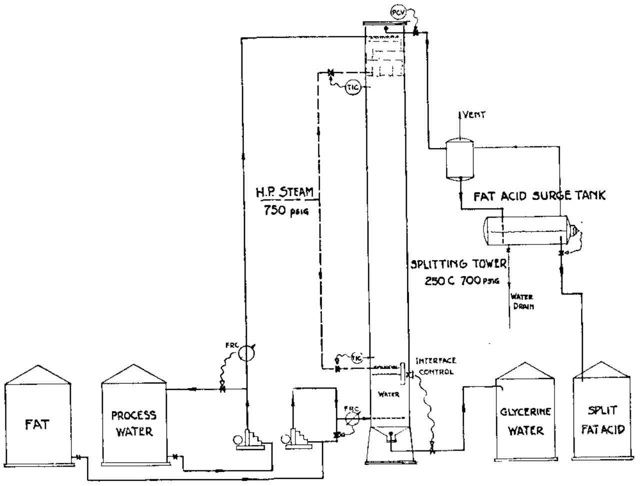

FIG. 2. Diagram of a Colgate-Emery fat splitter.

iliary equipment is not required, and bottoms handling is simplified, there are also advantages to non-catalytic splitting. The difference in throughput of a splitter with various amounts of catalyst added has been reported by K. Burrow (5). At a given water/oil input ratio in the column, and a fixed % glycerine in the fatty acids, the throughput of fatty acids can be increased from 3,600 lb/hr at 0.05% catalyst to over 6,000 lb/hr at 0.25% zinc oxide. The basic equipment for fat splitting is a tall, narrow autoclave. Preheated triglyceride oil is pumped into this vessel near the bottom and water near the top. The temperature employed is 450–500F, and the pressure, which must be high enough to keep the water liquefied, is in the 600–700 psi range. The fat is slowly converted to fatty acid as it rises through the column and passes out the top through an expansion chamber or flash cooler to storage before distillation. The water, falling in droplets down through the column by gravity, dissolves the glycerine liberated during the reaction and carries it out the bottom of the column as a dilute solution known as sweetwater. The crude fatty acids are collected and then distilled in a continuous still.

### Distillation

Continuous vacuum distillation of the crude fatty acids is carried out to remove residual fatty glycerides from the stream and to improve color and odor to the point where resultant fatty acids are suitable for soap making. Three types of stills are suitable for continuous distillation of fatty acids: The Lurgi design, the Mills modification of the Lurgi still, and semi-fractionating stills containing bubble-caps or sieve-trays in addition to the entrainment separations used in the Lurgi and Mills stills.

The Lurgi still is a steam distillation system in which the fatty acid and high pressure steam are fed into the central riser tube and vigorous ebullition ensues. The vapor impinges on an umbrella-type entrainment cowl, which returns unvaporized higher boiling material to an annular gallery containing high pressure steam coils. Here the high-boilers are vaporized and sent past a second entrainment separator. This still operates at 400F and 4 mm mercury pressure. It was the earliest of the continuous fatty acid distillation units and has been modified by many workers in this area since its development in 1922 (9).

The Mills still (Fig. 3) is a modification of the Lurgi still, and embodies the use of flash (dry) distillation rather than Lurgi's steam distillation principle. In addition the internal design of the Mills still uses two separate pot stills with entrainment separators rather than the annular heaters used by Lurgi. The fatty acid feed to the Mills still is preheated to about 450F and the operating pressure is approximately 3 mm of mercury.

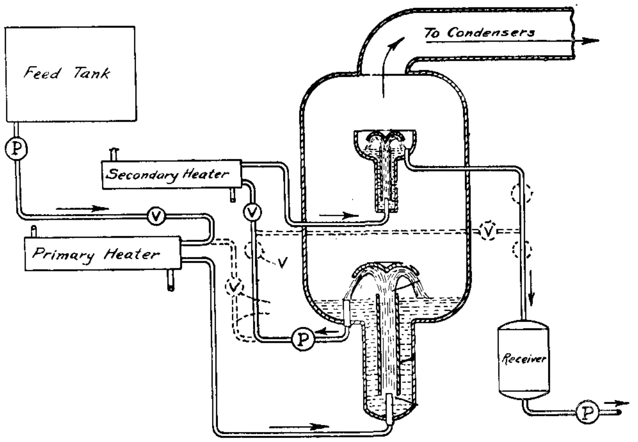

FIG. 3. Schematic diagram of a Mills continuous fatty acid still.

Column designs for the third type of still, the semi-fractionating type are similar to the fractionating still of Potts (10), (Fig. 4) but with fewer theoretical plates. This type of still is used to remove an "odor cut" for soap-making. These generally employ a certain amount of steam to minimize the effects of relatively long residence times in the still. The bubble cap or sieve-tray columns are employed when it is desired to remove a small amount of low-boiling material from the fatty acids, either to improve odor or to obtain short chain fatty acids for other applications.

### Hydrogenation

Improvement of color or odor stability of soaps is often accomplished by partial selective hydrogenation at some point in the process prior to saponification. The purpose of this step is to hydrogenate polyunsaturated linkages which are known to be the source of most rapid rancidity development. Hydrogenation is used primarily when inferior grades of animal fats are employed in soap-making, particularly in conjunction with the simpler continuous stills which do not remove an "odor-cut" of low-boiling fatty acids.

Hydrogenation in a continuous system can be of the fixed bed or fluidized bed type. More important perhaps is whether fats or fatty acids are to be hydrogenated. Hydrogenation of glycerides requires the use of less catalyst, but more careful pretreatment of fats is needed to prevent catalyst poisoning. Fatty acid hydrogenation may present problems related to removal of catalyst, but poisoning is less likely. Economic considerations and ease of processing will dictate the choice of method.

### Saponification or Neutralization of Fatty Acids

Neutralization of fatty acids with alkali metal hydroxides or carbonates is a straightforward and rapid reaction which readily lends itself to continuous or batch processing. It can be carried out in a variety of kettles, crutchers or other similar batch reactors or in continuous equipment in which the streams of fatty acid and alkali are controlled by a) flow meters (11), b) proportioning pumps connected by a variable ratio gear (5), c) viscosity of the resulting soap, or d) pH of the saponification mixture.

### Manufacturing Differences

A number of problems differing from those encountered in direct saponification of triglycerides result from following the fatty acid route to soap. These fall into the general categories of Raw Material Handling, Odor Stability and By-Product Utilization.

A. *Raw Material Handling.* In conventional soap boiling it is necessary to carry out much of the desired purification at the glyceride oil stage before charging to the kettle. The usual treatments involved bleaching of color with activated clay, or bleaching earths, often preceded by alkali refining to remove free fatty acids of bad odor from the fat. On the other hand, treatment before splitting is usually restricted to centrifuging or filtering to remove suspended inorganic and proteinaceous material. Washing with water or trisodium phosphate solution just prior to centrifuging is sometimes employed. Only simple pretreatment is needed since the primary purification stage in the fatty acid route is distillation of fatty acids. This direct, controllable purification stage eliminates other traditional procedures (such as repeated brine washes and removal of nigre phase) employed in soap boiling or continuous saponification.

Another aspect of raw material handling is mixing of fats and oils before splitting. Some manufacturers (5) mix oils before splitting, hence carry out the entire operation from splitting through distillation and saponification on mixed feed stock. It is also possible to split and distill tallow and coconut oil separately, mixing the distilled acids just before saponification.

In this procedure, larger "odor-cut" fractions can be removed from poor grade acids than from the better stocks, and the six and eight carbon acids can be removed from coconut fatty acids for further processing. The scheduling of splitters and stills becomes more complex when each glyceride raw material is handled separately rather than as a mixture.

B. *Odor Stability.* The problem of odor stability or rancidity prevention is a familiar one to most soap manufacturers. In many cases, antioxidants are added to toilet soaps to retard oxidation. This problem is particularly acute when fatty acids are prepared and used. Acids from animal fats are very sensitive to oxidation, and must be prevented from coming into contact with air. Inert gases are used to blanket distilled fatty acids before neutralization. In cases where prolonged storage of fatty acids is anticipated, antioxidants should be employed in addition to inert gas blanketing. When fatty acids are accidentally held for any length of time they are redistilled before saponification.

C. *By-Product Utilization.* The useful disposal of by-products is an economic necessity in most processes and soap-making is no exception. In conventional direct saponification nigre phase soap may represent up to 20% of the fat charged to the kettle, and must be cleaned up by washing or degraded to a lower quality soap. In the distillation of fatty acids, still overheads and bottoms constitute the principal by-products. Up to 2–3% of overheads and 10–12% of bottoms may be obtained.

Tallows overheads are used primarily in industrial soaps, but tallow bottoms or mixed stock bottoms could be recirculated to the splitter or still especially if catalytic splitting is employed. Recirculation to the splitter gives a savings in catalyst, since the zinc soaps remain in the bottoms. Recirculation to the still returns both heat and fatty acid. Eventually a zinc removal process is required. When non-catalytic splitting is employed, bottoms handling is simplified, since first run bottoms can be segregated and resplit separately to yield fatty acids of fair-to-good quality for blending with other fatty acids to make, for instance, a second quality toilet soap or good quality industrial soaps.

Another difference between fat saponification processes and the fatty acid route to soap is the ease of maintaining continuous analytical process control with the latter. Analysis of fatty acid mixtures (12) by gas chromatographic techniques provides good control on blends for soapmaking and on by-product fatty acids.

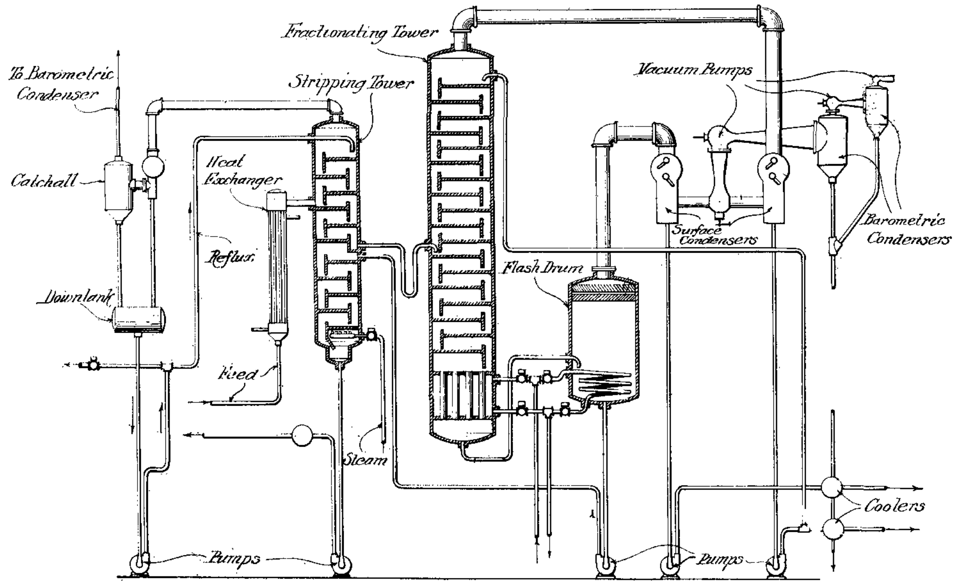

FIG. 4. Continuous fractionating still for fatty acids designed by Potts.

## Summary

Soap manufacture from fatty acids is a well established process with some advantages over continuous saponification of neutral fats. These include:

1) Ability to use cheaper fats.
2) Easier glycerol recovery.
3) Better control over by-products.
4) Versatility—fatty acids can be used to make other derivatives than soaps.

REFERENCES

1. Ittner, M. H., Colgate-Palmolive-Peet Co., U.S. 1,918,603 (1933); U.S. 2,139,589 (1938); U.S. 2,221,799 (1940); U.S. 2,435,745 (1948); U.S. 2,458,170 (1949); U.S. 2,480,471 (1949).
2. Emery Industries Inc., U.S. 2,486,630 (1949); British Patent 594,141 (1947).
3. Mills, V., Procter and Gamble, U.S. 2,156,863 (1939); U.S. 2,159,397 (1939); U.S. 2,233,845 (1941); British Patent 482,535 (1938); Canadian Patent 365,544 (1937).
4. Schulerud, A. L., JAOCS, *40*, 609–615 (1963).
5. Burrow, K., Trans. Instn. Chem. Engrs.*31*, 250–261 (1953).
6. Allen, H. D., et al., Chem. Eng. Prog. *43*, 459 (1947).
7. Barneby, H. L., and A. C. Brown, JAOCS, *25*, 95 (1948).
8. Lascaray, L., Fette u. Seifen, *46*, 628 (1939); Ind. Eng. Chem. *41*, 786 (1949); Seifensieder—Ztg., *64*, 122 (1937).
9. Lurgi Gesellschaft fuer Waermetechnik. German Patent 392,874 (1922).
10. Potts, R. H., U.S. 2,322,056 (1943).
11. Ledgett, U.S. 2,594,461.
12. Beck, E. C., E. Jungermann, and W. M. Linfield, JAOCS, *39*, 53–55 (1962).

---

# Continuous Sulfonation Techniques

**S. J. SILVIS and MARIO BALLESTRA, Ing. Mario Ballestra & Co., S.p.A., Milano, Italy**

THE SULFONATION of alkyl benzene and the sulfation of fatty alcohol have been under continuous study not only by the detergent manufacturers, but also by the suppliers of detergent manufacturing equipment and of detergent raw materials.

When detergents were first introduced to the market they were generally in powder form and the active ingredients employed could contain large amounts of sodium sulfate without presenting any undue problems. However, with the advent of the liquid products, active ingredients containing little inorganic salt were essential—and it is this fact which has stimulated, to a major extent, the development work on sulfonating with $SO_3$ rather than with oleum.

I think that it will be worth a few minutes of our time to follow briefly the development of the sulfonation process so that we might better appreciate the problems that had to be overcome to arrive at the present stage—that is, sulfonation using gaseous $SO_3$ produced directly from the burning of sulfur.

Throughout this discussion keep several points in mind:

1) Product quality is the key to the acceptability of a process, and for alkyl benzene the specifications are: 98% completion of reaction and a white paste upon neutralization with the alkali.
2) The color of the neutralized paste is good or bad depending upon the ability of the process to remove the heat of reaction instantaneously.
3) The heat of reaction for the sulfonation increases with increasing oleum strengths—and is a maximum when $SO_3$ is used.

Thus it is easy to understand that the first production units were batch plants and the sulfonating agent was 10–20% oleum. In these plants the alkyl benzene was weighed and placed in a tank; then the oleum was slowly added until the quantity required by the formula was also placed into the tank. With the two reactants now intimately mixed, they were now permitted to digest for 30–45 min. After the digestion period the neutralization of this acid mix was carried out.

Continuing engineering development work—to more efficiently remove the heat of reaction at the point of contact of the oleum with the alkyl benzene—soon permitted the use of 25% oleum.

The next stage in the development of the sulfonation process was that of continuous processing rather than batch. Here the only advantages were possibly lower plant costs and lower operating costs, since there was not any improvement in product quality.

Later came High Active Ingredient (AI) which allowed the separation of the major portion of the sulfuric acid present in the acid mix prior to neutralization. Product with an active content of 87–88% on a dry basis can be produced by such a process.

But many liquid formulas demanded still higher active contents. The advent of stabilized liquid $SO_3$ made it possible to economically prepare a product with 96–97% AI on a dry basis. The suppliers of this stabilized liquid $SO_3$ developed batch processes which included the vaporization of the liquid $SO_3$, diluting this with dried air to approximately 10% by volume, and contacting this gaseous stream with alkyl benzene previously weighed and placed in the reactor tank. Although the use of liquid $SO_3$ has economic advantages over the use of oleum, it was the inability of this process to match the product quality produced on the oleum plants that prevented it from being readily accepted by the major detergent manufacturers. It should be mentioned that there is one manufacturer who claims to have a continuous process using vaporized $SO_3$ but there are no details available on this.

There is another batch process operating today which uses the technique of reacting liquid $SO_3$ with alkyl benzene in the presence of liquid $SO_2$—and conducting this reaction at very low temperatures. The product produced by this process is excellent. Mr. Morrisroe pioneered the commercial development of this process.

Now we come to the latest stage of development for the sulfonation reaction—and this is the burning of sulfur to produce the required $SO_3$ and coupling this directly to the sulfonation reactors for continuous operation.

This combination of sulfur burning and sulfonation has economic advantages and has been worked out to a high degree of precision by the Ing. Mario Ballestra Co. There are others who have followed this type of processing and we will attempt to show the basic differences between various processes. Very few details are available concerning other processes. Therefore our attempt to compare other opera-