Degumming and Refining Practices in Europe

BEN BRAAE, Manager, Fats and Oils Processing Division,
Alfa-Laval AB, Tumba, Sweden

ABSTRACT

European practices for degumming and refining various vegetable oils are reviewed. Special attention is given to specific processes differing from those commonly used in the U.S. and to the practical problems of day-to-day operations.

In some respects, degumming and refining practice in Europe differs from that in the U.S. The first of two main reasons for these different practices is, on the one hand, that many U.S. refineries treat only one or two oils—normally soybean and/or cottonseed oil, the local production of which is more than sufficient to cover the consumption of vegetable fat inside the country—whereas in Europe the majority of fatty oils (or correspondent seeds) have to be imported, and a typical European refinery is equipped to treat all kinds of oils dependent on their momentary availability and price. On the other hand, the second reason is that the quality of the imported seeds or oils is sometimes bad, especially during wars and blockades, and the acidity is higher than for the oils treated in the U.S.

When, for instance, an integrated oil mill and refinery is solvent extracting and refining only soybean oil, the extracted oil may be refined immediately after the extraction, without intermediary storage tanks, thus securing a fully continuous operation. It should be noted that the two kinds of oilseeds mainly treated in the U.S. are precisely those which are solvent extracted directly without pre-pressing because the oil content of these seeds is relatively low.

For oilseeds with high oil contents, a combination of pre-pressing and solvent extraction is widely regarded as the most economical way of extracting the oil. This method of operation necessitates storage tanks for the different types of crude oils and especially so when different types of seeds are extracted in the same plant.

Most solvent extracted oils contain considerable amounts of phosphatides and other mucilaginous materials which during storage form deposits in the storage tanks. Such products are difficult to handle, especially as oxidation and polymerization may occur. The tank residues include considerable amounts of oil and therefore cause high oil losses. A high gum content of the crude oil also increases refining losses considerably, as the gums will emulsify a considerable amount of neutral oil which is lost in the soapstock. Furthermore, the splitting of the soapstock with sulphuric acid is extremely difficult when great amounts of gum are present. Therefore, it is customary in Europe to carry out a degumming of the solvent extracted oil prior to caustic refining.

A separate degumming operation is, however, not necessary for expeller pressed oils. Degumming is carried out immediately after stripping of the solvent by adding a small amount of water, approximately equal to the amount of gums, which precipitates the gums dissolved in the oil.

Figure 1 diagrams an industrial degumming plant. The preheated oil is mixed with water, passed through a mixer giving a holding time of 10-15 min, and then goes to a centrifugal separator, where the gums are separated from the oil. If the crude oil is going to be stored before further processing, vacuum drying is added to prevent hydrolysis of the oil during storage. Gums leaving the separator contain 50-60% water, while the dry matter contains ca. 25% ± 10% oil. Care should be taken to add only the amount of water necessary to precipitate the gums, as any excess water causes unnecessary oil losses. Oil leaving the separator normally contains 0.2-0.3% nonhydratable gums, but certain crude oils contain 2 or 3 times that amount, which cannot be precipitated by water.

In the removal of phosphatides from certain crude oils, especially soybean oil, salable lecithins can be obtained. In this case, the lecithins are dried and sometimes also purified by extraction with acetone and bleached with hydrogen peroxide. In most other cases, the gums can be added to the meal cakes. Even when the bulk of the gums is removed before caustic refining, the losses during the latter treatment depend greatly on the working conditions. In the conventional batch refining process, the inherent limitation is that the same condition which reduces emulsification and contributes to the removal of foreign matter such as gums and pigments, i.e., the use of strong caustic, also increases the saponification losses because any excess caustic soda is consumed in saponification of the neutral oil due to the long contact time between oil and caustic prevailing in the batch process.

In the continuous process made possible by the use of centrifuges, this contact time and, consequently, the refining losses, are considerably reduced. The first continuous process, the straight caustic process, was developed in the U.S., where two oils alone, soybean oil and cottonseed oil, dominate the production of vegetable fats for human consumption. Limiting production to mainly two kinds of oil, taken in conjunction with the then relatively large overall capacities of the American refineries and the high level of wages, did much to pave the way for the introduction of the continuous refining process, as this was found to offer considerable economies in running cost.

In the straight caustic process, the caustic and the oil are mixed at room temperature and then treated to break the emulsion formed at the low reaction temperature. The mixture then goes to a centrifuge, where the soapstock is separated from the oil. The oil is then washed with water, and the soap containing water phase is again separated from the oil in another centrifuge (Fig. 2). As a rule, the quantity of caustic used in this process greatly exceeds the quantity necessary for neutralization of the fatty acids. This is because a considerable excess of caustic is necessary to ensure complete removal of phosphatides and pigment at the low reaction temperature, especially for nondegummed oils. As the contact time between oil and caustic is relatively long—ca. 5-10 min—considerable saponification losses arise. After the war, a new continuous caustic refining process, the Short-Mix process, was introduced in Europe, where the relatively high acidity of many oils made it

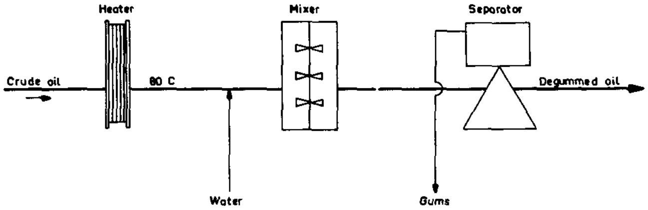

FIG. 1. Industrial degumming plant.

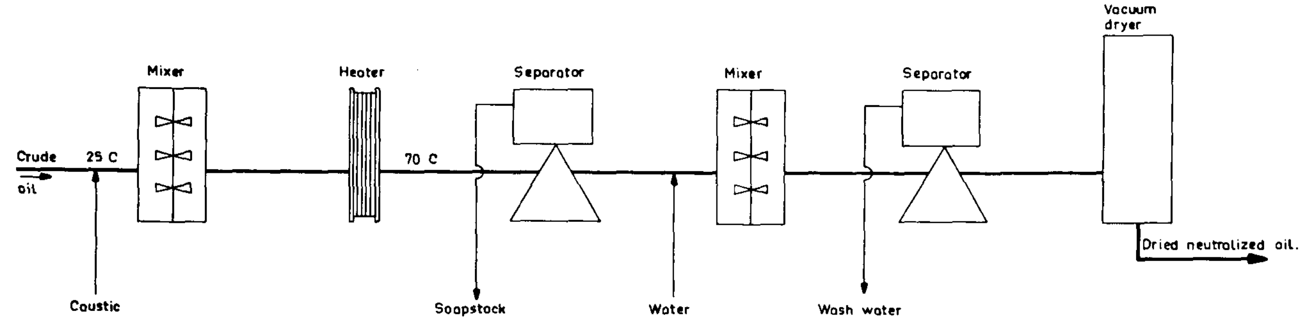

FIG. 2. Straight caustic refining process.

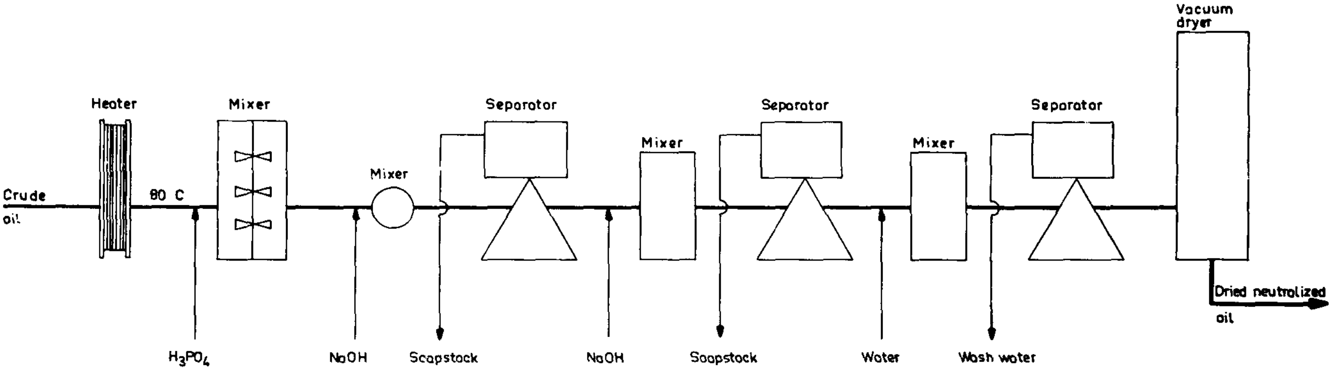

FIG. 3. Short-Mix caustic refining process.

necessary to avoid the long contact time and the big excess of caustic used in the straight caustic process.

In the Short-Mix process, oil is heated to a temperature of 75-90 C before the addition of caustic soda. An immediate break between oil and soapstock therefore takes place, thus reducing the emulsification losses. At the same time, the contact time between oil and caustic is only ca. 30 sec, so that the saponification losses are also reduced.

Because solvent extracted oils are always degummed prior to caustic refining, and because a pretreatment with phosphoric acid, which removes the last traces of nonhydratable phosphatide, is standard procedure in Europe, it is not necessary to use the big excesses of caustic normally used in the straight caustic process. In the case of cottonseed oil and some other oils with bad color, a second caustic treatment is used, but as the bulk of the soapstock has been removed, the losses are relatively small. The oil is finally washed with demineralized water to remove the soap.

The principle of the Short-Mix process is shown in Figure 3. Furthermore, a hermetic disc-type separator is used for the separation of soapstock and wash water from the oil (Fig. 4). Both the inlet and the outlet of the hermetic separator are fitted with axial seals so that the machine forms a completely closed system together with all apparatuses connected to it. The mixture of oil and soapstock is introduced into the bowl under pressure through the hollow rotating separator spindle. This constitutes a very mild treatment of the reacting materials and reduces the risk of particle breakup and emulsification and avoids any admixture with air.

When using centrifugal separators for refining fatty oils, it must be taken into consideration that even the biggest separator has a sludge space of only ca. 15-20 liters, whereas the amount of oil passed through the bowl is between 50 and 300 tons/24 hr. Even very small amounts of solid materials with a higher specific gravity than the soapstock will therefore clog the bowl after a certain time of operation. Such solids may be fine parts of the shells from the nuts or the seeds which have not been completely removed by filtration of expeller pressed or solvent extracted oils. By the phosphoric acid treatment, the natural calcium and magnesium content of many oils—especially soybean and rapeseed oil—is precipitated as insoluble phosphates with a high specific gravity. Calcium and magnesium carbonate may also be present, especially if hard water is used for preparing the caustic or as wash water.

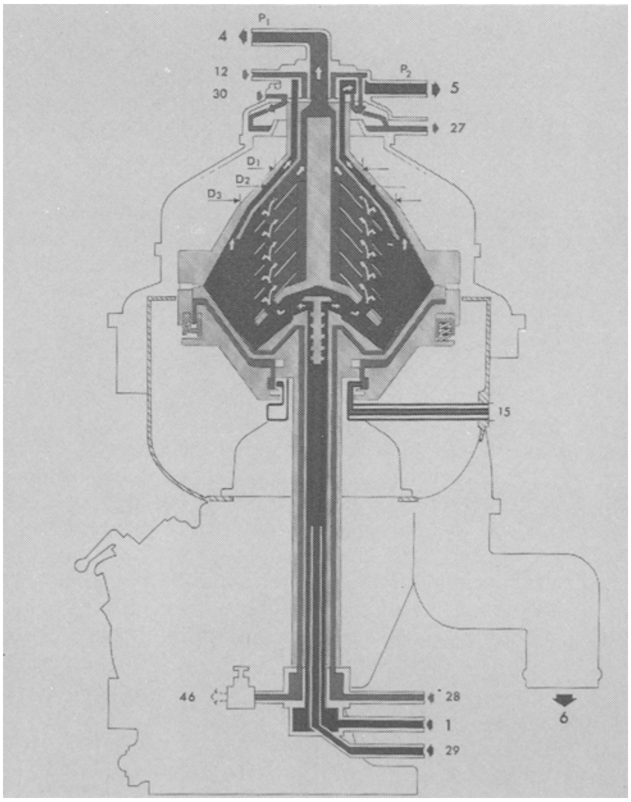

FIG. 4. Hermetic disc-type self-cleaning separator.

The latest development is a separator which is both hermetic and self-cleaning (Fig. 4). The bowl of this solidejecting separator is divided into two parts, upper and lower. When the bowl is in normal operation, the lower part is pressed against the upper part by a separate sliding bowl bottom to which water pressure created by the centrifugal force is applied. Due to a gasket between the two parts of the bowl, this is kept tight until the water pressure is removed, when the lower part falls down a few millimeters, opening a ring-formed slit around the bowl. The sludge is then thrown out together with some soapstock. The opening of the bowl can be regulated in such a way that only sludge and some soapstock are lost but absolutely no oil, and it is not even necessary to stop the feed to the separator when the solids are ejected. As the amount of sludge is normally relatively small, opening the bowl needs to be done only at intervals of ca. 1/2-1 hr, which can be regulated by a timing device.

The advantages of the Short-Mix process as compared to the straight caustic process, especially for oils with high acidity, are shown in Table I.

Under the conditions prevailing during Short-Mix refining, the amount of neutral oil emulsified in the soapstock is reduced when the excess caustic is increased, whereas the saponification losses are increased. The overall loss passes a minimum, normally when ca. 30% excess of caustic over the stoichiometrically calculated amount is used. Losses obtained when Short-Mix refining peanut oil with various excesses of caustic illustrate this point (Table II).

As is also seen in Table II, the saponification losses increase much more rapidly when refining palm oil or other oils which are easily saponified, and there is no minimum of losses at any excess of caustic.

For palm oil and other oils with high acidity, the losses can, however, be further reduced by using the Ultra-Short-Mix method. In this, the caustic soda is introduced directly into the hollow separator spindle, where a special mixing device is located (Fig. 4). The very short contact time allows use of considerable excess of strong caustic without excessive saponification. As can be seen from Table III, considerable improvement of the yields is obtained when refining palm oil by the Ultra-Short-Mix method instead of the Short-Mix method.

Due to saponification of neutral oil, the refining losses cannot be calculated from the oil content of the acid oil obtained by splitting the soapstock with mineral acid. The best way of determining the overall loss is by weighing the ingoing crude oil as well as the dry neutralized oil. As the absolute loss does, of course, depend on the acidity of the crude, it is customary in Europe to express the loss as refining factor, i.e., the total loss divided by the fatty acid content. In this way, the refining efficiency when refining oils with different free fatty acids (FFA) may be directly compared. Obviously, the refining factor will depend on the amount of impurities other than fatty acids in the crude oil. If the amount of water, gums, and other impurities is high in proportion to the FFA content, the refining factor will, of course, be high. Experience with all kinds of oils shows that the refining factor obtained in practice with properly filtered and degummed oils varies between 1.4 and 1.7.

For many oils with a low content of nonglycerides other than fatty acids, refined oil of adequate quality is obtained by simple Short-Mix refining and a single water wash. When using the disc-type hermetic separator, a soap content of ca. 50 ppm is obtained by a single water wash and below 10 ppm with double water wash, provided demineralized water is used.

It has been known for a long time that certain oils, especially soybean and rapeseed, contain phosphatides which cannot be removed completely even by repeated treatment with caustic soda. When present during bleaching and especially deodorization, these residual phosphatides cause poor taste and low oxidation stability of the deodorized oils. Complete elimination of these phosphatides can,

TABLE I

Refining of Cottonseed Oils with Different Acidity: Comparison between Straight Caustic and Short-Mix Processes

	Free fatty acid in crude oil (%)	Excess caustic (%)	Loss in neutralization (%)	Loss in rerefining (%)	Loss in water wash (%)	Total loss (%)
Straight caustic process	1.0	200	2.2	—	0.3	2.5
	5.0	200	11.0	—	0.3	11.3
Short-Mix process	1.0	25	1.7	0.6	0.3	2.6
	5.0	25	8.5	0.6	0.3	9.4

TABLE II

Losses by Short-Mix Neutralization of Peanut and Palm Oils[a]

	Peanut oil: 4.0% free fatty acid				Palm oil: 5.1% free fatty acid			
Excess caustic (%)	Total loss (%)	Neutral oil in acid oil (%)	Neutral oil loss in soapstock (%)	Oil loss by saponification of neutral oil (%)	Total loss (%)	Neutral oil in acid oil (%)	Neutral oil loss in soapstock (%)	Oil loss by saponification of neutral oil (%)
0	8.11	49	3.98	0.13	9.40	45	4.23	0.07
20	6.84	38	2.60	0.24	9.10	35	3.18	0.82
40	5.42	15	0.89	1.03	9.35	30	2.80	1.45
60	6.45	9	0.53	1.92	9.90	25	2.48	2.32

[a] Temperature 80 C, concentration of caustic 24° Bé, contact time 30 sec.

however, be obtained by treating the oils with a small amount of concentrated phosphoric acid prior to neutralization, as may be seen from Table IV. The mineral acid is neutralized together with the fatty acids, and the amount of caustic is calculated correspondently. The phosphoric acid also acts as a sequestering agent, combining with metal ions in the oil. This is important because such ions, especially copper and iron, are strong catalysts for oxidation of the oil.

A further advantage of using hermetic separators is that the risk of oxidizing during refining is eliminated; an all-hermetic plant is, in fact, a completely closed system, where the oil has no contact with air from the moment the crude oil is pumped into the plant until the neutralized and dry oil leaves the drying system. The difference in degree of oxidation when the oil is refined by the conventional batch refining system in contact with air and when refined in an all-hermetic Short-Mix plant is shown in Table V.

As is well known, the first oxidation products are peroxides, which later (particularly when the oil is heated to high temperatures during bleaching and deodorization) are broken down to unsaturated aldehydes, which give rise to bad flavor and poor stability of the finished oil.

The total oxidation value is conveniently expressed as "totox" value, which is equal to 2 times the peroxide value plus the anisidine value, the last mentioned being a measure of the carbonyl content of the oil.

As mentioned, the peroxides are destroyed during deodorizing, but even a slight increase in oxidation has a considerable effect on the keeping quality of the deodorized oil, as clearly shown in Figure 5. Here the time necessary for reaching a certain peroxide value of the deodorized oil under well-defined oxidation conditions (65 C and blowing with air) is plotted against the peroxide value of the neutralized oil. As is seen, an increase in the peroxide value of neutralized soybean oil of only 1.2 meq/liter is enough to reduce the time needed to reach a certain peroxide value by oxidation of the deodorized oil by ca. 50%.

Another refining method, used by a number of refineries in Europe, is the Zenith process (Fig. 6). After a pretreatment with concentrated phosphoric acid, followed by a sludge removal if necessary, the oil is neutralized as droplets, rising by gravity through a lye column. The alkali lye is weak and keeps the formed soap in solution. This eliminates almost entirely the formation of emulsion and saponification of neutral oil. Water washing of the neutralized oil is not necessary. It is claimed that the yield, especially on certain oil sorts, is very much improved and that the quality of the refined oil is excellent. The three-step line, including vacuum bleaching, is delivered in sizes 2-10 tons/hr.

A process closely connected with caustic refining is splitting the soapstock with sulphuric acid. This operation has conventionally been carried out in batch containers, either iron vessels clad with lead to prevent corrosion or vessels made of acid resistant ceramics. Due to bad contact between soapstock and acid, a big excess of strong sulphuric acid was used, and consequently the vessels used needed costly repairs and the acid oil was burnt or sulphonated.

A continuous process for soapstock splitting is shown in Figure 7. The splitting is most easily carried out when the TFM of the soapstock is low, preferably not higher than 10%. In a continuous process, this is easily done by retaining part of the acid water. The sulphuric acid is added by means of a piston-type dosing pump, and, as the pump has two pistons, water can be added to dilute the sulphuric acid prior to contact with the soap. Any burning, sulphonation, or discoloration of the acid oil is therefore easily avoided.

The soapstock and sulphuric acid are mixed in a small, separate mixing tank from where it passes to a plastic decantation tank. This decantation tank has three different functions. First, many types of soapstock need a certain

TABLE III

Neutralization of Palm Oil with 7.5% Free Fatty Acid Content in Short-Mix and Ultra-Short-Mix Refining

Mixing method	Contact time before separation (sec)	Caustic concentration (° Bé)	Excess caustic (%)	Mixing temp. (C)	Total loss (%)	Refining factor
Short-Mix	30	20	5	80	13.9	1.86
Short-Mix	30	20	50	80	16.3	2.18
Ultra-Short-Mix	0.2	28	5	80	12.9	1.72
Ultra-Short-Mix	0.2	28	50	80	11.6	1.55

TABLE IV

Influence of Residual Phosphatide Content in Neutralized and Bleached Oils on Oxidation Stability and Flavor of Deodorized Oils

Type of oil	Treatment other than caustic neutralization	Peroxide value before bleaching (meq/liter)	Phosphatide content in bleached oil (%)	Oxidation stability of bleached deodorized oil expressed as peroxide value (meq/l) after oxidation at 60 C				Flavor score
				100 hr	200 hr	300 hr	500 hr	
Rapeseed oil	None	4.35	0.111	22.8	40.5	–	–	1
Rapeseed oil	Pretreatment with 0.15% conc. H_3PO_4	4.54	0.01	2.1	3.0	2.8	2.5	5
Soybean oil	None	2.05	0.108	30	–	–	–	1
Soybean oil	Pretreatment with 0.15% conc. H_3PO_4	1.53	0.001	1.4	4.3	10.4	32.1	5
Soybean oil	None	7.81	0.02	2.0	3.5	4.8	5.4	1
Soybean oil	Pretreatment with 0.15% conc. H_3PO_4	9.05	0.02	1.5	1.7	1.7	2.4	5

TABLE V

Increase in "Total Oxidation"[a] during Batch Refining and Continuous, All-Hermetic Refining

Kind of oil	During batch refining (peroxide units)	During continuous, all-hermetic refining (peroxide units)
Rapeseed	+ 1.5	+ 0.1
Soybean	+ 2.2	- 0.2
Peanut	+ 2.8	+ 0.3
Cottonseed	+ 4.0	–

[a] "Totox" value = 2 x PV (peroxide value) + anisidine value.

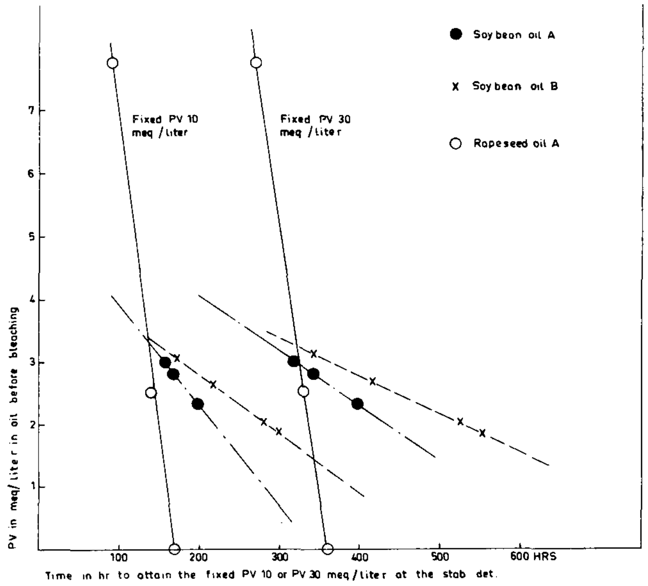

FIG. 5. Relationship between increase in peroxide value during caustic refining and oxidation stability of deodorized oil.

reaction time, not for the splitting of the soap itself, a reaction which is practically instantaneous, but for settling and breaking the emulsion formed due to the presence of phosphatides, proteins, and other mucilaginous substances. Second, the amount of water going to the separator is much greater than the amount of acid oil, and, if the separated water should have a low fat content, the separator must be dimensioned according to the amount of water fed to it and not to the amount of acid oil. Therefore, the bulk of the acid water is siphoned off from the decantation tank, and only the acid oil containing a small amount of water and mucilaginous substances is passed to the separator, which is of the self-cleaning type, so that solids can be automatically discharged from the bowl. Third, the purpose of removing the bulk of the water before going to the centrifuge is to make a final water wash of the acid oil possible. Extra wash water is added to the acid oil, which will therefore not contain sulphuric acid when leaving the separator. This is important if acid oil is going to be stored or transported in vessels of iron, stainless steel, or aluminum, or if it is going to be distilled.

Experience has shown that good splitting and settling can be obtained at a pH of ca. 3.5. The plant can, of course, be provided with automatic pH control. Some kinds of soapstock, as, for instance, soapstock from nondegummed soybean oil or from sunflower oil, do create emulsions which are extremely difficult to break. It has been found that addition of small amounts of ethyl-hydroxyethyl-cellulose (trade name Modocoll) breaks the emulsion very efficiently. Calculated on the amount of acid water, the concentration of Modocoll needs to be only 50-100 ppm. Casein has much the same effect as Modocoll but is considerably more expensive.

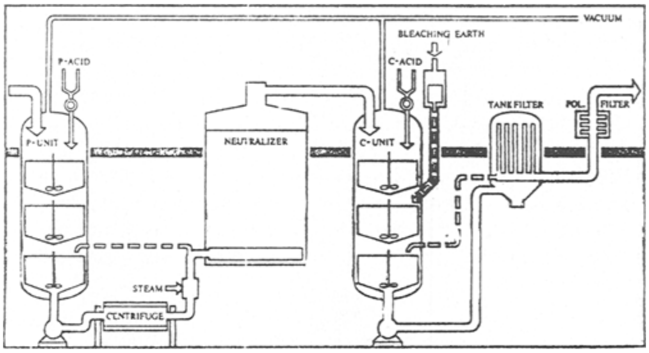

FIG. 6. Flow chart of Zenith refining process.

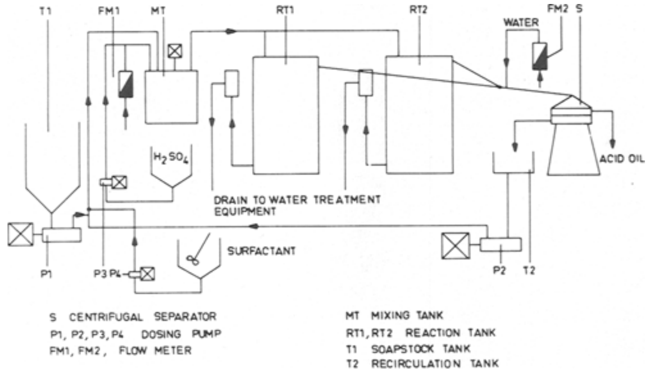

FIG. 7. Continuous soapstock splitting plant conceived for soapstock from sunflower oil.

In most of Western Europe, acid oil must be distilled before the fatty acid can be used. When the acid oil was obtained from soapstock from batch neutralization, the oil content of the acid oil was so high, often 40-50%, that the soapstock was hydrolyzed with water in autoclaves partly to recover the glycerol and partly to get an acid oil with a high FFA content so that the distillation losses would be reduced. As the soapstock from centrifugal refining has only half the amount of neutral oil as that from batch refining, the autoclave splitting of the acid oil is hardly a paying proposition, and it is better to make a complete saponification of the soapstock prior to the splitting with sulphuric acid. Using temperatures of ca. 150 C, the soapstock can be completely saponified, and most of the phosphatides are saponified at the same time, thus making the splitting much easier, and an acid oil with 98% FFA can be obtained whereby distillation losses are reduced to a minimum.