Quality of Byproducts from Chemical and Physical Refining of Palm Oil and Other Oils

WONG MONG HONG, Lam Soon Oil & Soap Manufacturing Pte. Ltd., 161 Jalan Jurong Kechil, Singapore 2159, Republic of Singapore

ABSTRACT

Being byproducts, palm soapstock, palm acid oil and palm fatty acid distillates (PFAD) have a wide range of quality and composition. They also consist of many impurities and minor components. Due to development of refining techniques. PFAD have largely replaced palm acid oil, especially in the producing countries. Although both palm acid oil and PFAD can be used for making low-quality laundry soap directly, they are often subjected to further treatment. They have found many industrial applications, especially in the feed and fatty acid industries. Quality of recovered oil from spent earth can be as good as bulk of the bleached stock if proper solvent such as hexane is used for extraction. Spent earth can also be used for incineration to produce energy, cattlefeed and landfill.

INTRODUCTION

The main byproduct of chemical refining is called soapstock (oil foot); when acidulated with dilute sulfuric acid, it becomes acid oil. The main byproduct of physical refining, on the other hand, is known as fatty acid distillates. Apart from these, spent bleaching earth is also produced as byproduct in both modes of refining.

It is not an easy task to describe the quality and composition of byproducts. In general, all process and quality controls of an operation are designed for main products. Only the undesired and unwanted components will go to form byproducts. As a result, we would expect acid oil, fatty acid distillates and spent earth to have a vast range of composition and quality, and contain many minor components and impurities.

BYPRODUCTS FROM REFINING OF PALM OIL PRODUCTS

Owing to the tremendous increase of crude palm oil production during the past one-and-one-half decades, revolutionary progress had been made on palm oil technology, especially in processes such as fractionation, refining and some end applications. But research on byproducts was much neglected. This might be due to the fact that our oil technologists were much involved in the developmental work of palm oil itself. In the meantime, there was no urgent need to upgrade these byproducts because reasonable return had been achieved from the investment of palm oil processing. Nevertheless, the picture today is quite different. Apart from perfecting palm oil fractionation and refining technology, the question on how to lower processing costs in the palm oil industry is probably the most pressing issue for all the refiners if they are to continue their business in the very competitive international oil and fat market. If we can increase the value of byproducts, the overall refining costs will be reduced and substantial contributions can be made to the survival of the entire industry. This indeed is one of the main intentions of this paper.

Quality and Composition of Palm Soapstock and Palm Acid Oil

During the neutralization reaction of caustic soda and/or soda ash with crude palm oil in chemical refining, palm soapstock is produced as what is known as 'foot' (see Fig. 1). The quality and composition of the various types of palm soapstock depend mainly on the type of processing equipment, the concentration and type of neutralizing agents, the operating conditions, the quality and grade of feestocks and finished products. The common specifications of palm soapstock are given in Table I. Except for the iodine values, all numerical specifications of soapstock derived from palm oil, palm olein and palm stearin seem identical. But in practice, they have some differences. The oil losses of refining palm stearin and sometimes palm oil are generally higher than that of palm olein, which leads to a comparatively lower FFA percentage in soapstock of palm oil and stearin. This may be because of the smaller density differences between palm oil or stearin and soapstock as compared to that of palm olein, which causes additional difficulties in the separation of palm oil or stearin from soapstock, irrespective of whether the means of separation are centrifuging or gravitational settling. Nevertheless, the content of free fatty acids (FFA) in the fatty matter portion of palm soapstock should remain between 55-70% for proper operation. If FFA content does go beyond this range, it may indicate that some of the steps in neutralization are not quite in order. Over- or under-saponification, excessive entrainment and/or emulsification may have occurred. Alfa-Laval has proposed the use of a specially formulated chemical to recovery neutral oil in soapstock. The treatment is known as Halvopon Or process (1). Unfortunately, this process has so far been used for the refining of more expensive fats such as cocoa butter only. De Smet (2) has also developed a miscella refining process for crude oil within the solvent extraction plant prior to solvent removal. Caustic soda is added to the miscella for neutralization and soapstock is separated by high speed centrifuge. This method claims to have less neutral oil losses in soapstock and more effective removal of phosphatides and pigments from oil phase to soapstock. No water washing step is required. Of course, all the costs and precautions associated with solvent handling are present in this method.

The unsaponifiable matters tend to be concentrated in palm stearin during fractionation. This is reflected in the composition of its soapstock. Some refiners may like to produce dilute soapstock which is easier for pumping and handling, while others may like to produce a more viscous soapstock which has less moisture. According to international trade practice, soapstock is sold on the basis of 50% total fatty matter (TFM). If TFM in soapstock happens to fall below 35% (in some cases 30%), shipments can be rejected (3,4). Due to high transportation costs, trading of this product in the international market is practically nonexistent. Palm soapstock can be used to make low-quality soap directly, especially when the soap plant is near or within the battery limit of the refining plant, so that transfer can be made by pumping. This is often practiced in some of the developing countries where inexpensive laundry soaps are still in demand. Soapstock can also be treated with sulfuric acid which neutralizes the soap and separates out the large quantity of water to produce palm acid oil.

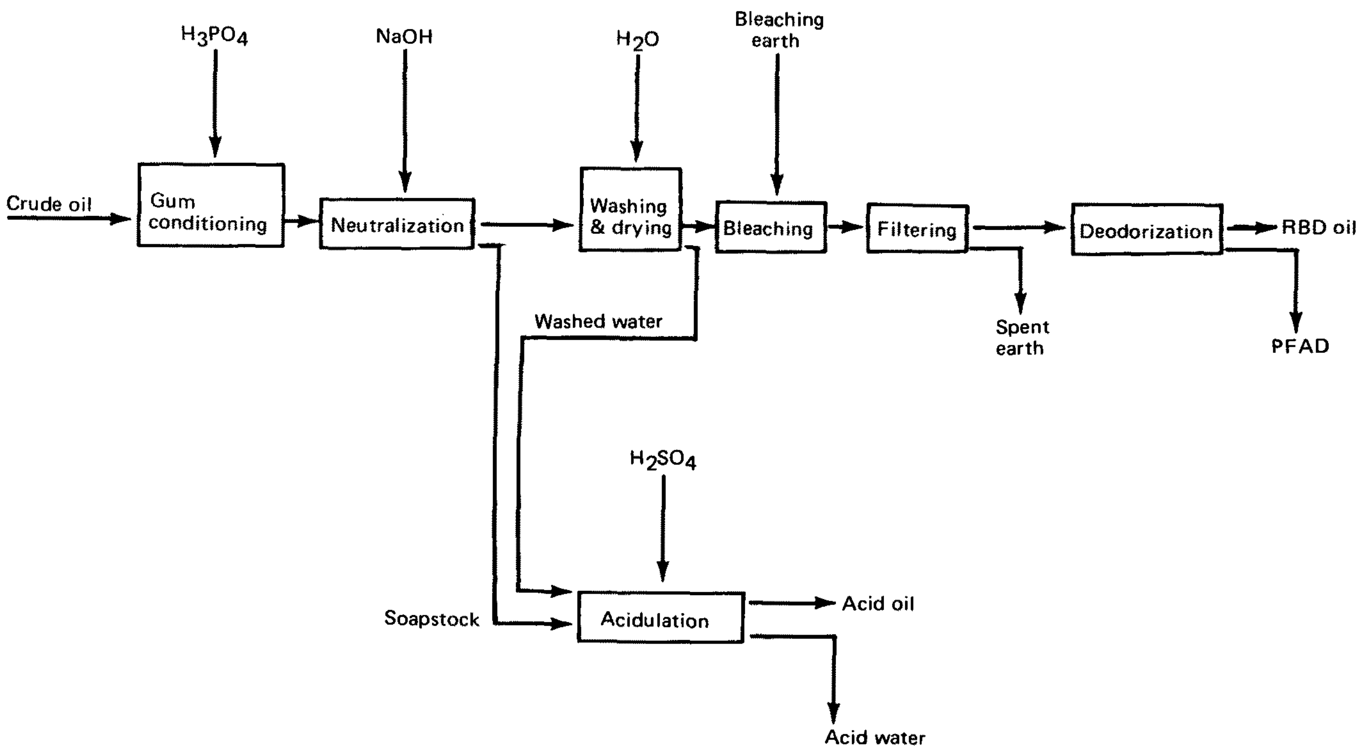

FIG. 1. Alkali (chemical) refining process.

TABLE I

Typical Specifications of Palm Soapstock

	From palm oil	From palm olein	From palm stearin
TFM (%)	25.0-50.0	25.0-50.0	25.0-50.0
Moisture (%)	50.0-75.0	50.0-75.0	50.0-75.0
Unsaponifiable matters (%)	0.3- 1.5	0.3- 1.5	0.3- 1.5
IV	51.0-55.5	57.5-60.0	36.0-48.0

As acidulation process is well documented in the literature and is commonly practised by industry today, it is not the intention here to go into details except for a few words of caution. Soapstock must be processed as soon as possible after it is produced so that chances of fermentation and emulsification are minimized. As acidulation process involves conditions of high temperature (110-130 C) and dilute mineral acids (pH 2.0-3.5), corrosion and maintenance costs for both processing equipment and effluent drainage can be the prime cost factors to be concerned. Any step taken to recover residual sulfuric acid from acid water will definitely reduce the final costs of acid oil production.

Acid oil is essentially the fatty portion of soapstock. The moisture content has been reduced to 1-2%. Common specifications of various types of palm acid oil are given in Table II. More often than not, acid oil is produced for the reason of moisture removal so that a smaller volume is obtained for handling or storage. It will also have less chance for fermentation and emulsification, cheaper cost for transportation and greater ease for subsequent treatments. This is particularly necessary when downstream processing is not within the battery limit of the refining plant. In commercial practice, acid oil is traded on 95% TFM basis; shipments can be rejected if TFM goes below 85% (3,4).

As alkali refining removes nearly all phosphatides which are originally present in traces in crude palm oil, these compounds are transferred to palm soapstock and at least partly to palm acid oil. Other caustic reactive materials such as carbohydrate and protein fragments may also be transferred to palm soapstock and palm acid oil because of their relative solubility, although we have yet to identify the nature of these fragments and their degraded products. Carotenoid pigments, on the other hand, are probably physically absorbed by the soap formed, rather than by chemical combination. Since soap has only limited absorptive capacity, the reddish color of crude palm oil is only lightened but not removed by caustic refining. About 10-15% of tocopherol (α form) and tocotrienol (α, γ, δ forms) are also removed by physical absorption of soap. Due to the relative solubility of soap in water, the residual soap content in palm oil is normally in the region of 0.03-0.30%. Hence a good proportion of carotenoid pigments, tocopherol and tocotrienol which remain in acid water will be washed away instead of being transferred from palm soapstock to palm acid oil.

TABLE II

Typical Specifications of Palm Acid Oil

	From palm oil	From palm olein	From palm stearin
FFA (%)	55.0-75.0	55.0-75.0	55.0-75.0
TFM (%)	95.0-97.0	95.0-97.0	95.0-97.0
Moisture (%)	1.0- 2.0	1.0- 2.0	1.0- 2.0
Unsaponifiable matters (%)	1.0- 3.0	1.0- 3.0	1.0- 3.0
IV	51.0-55.5	57.5-60.0	36.0-48.0
Titre (C)	38 -45	19 -26	44 -51

Palm soapstock is a rich source of vegetable sterols which may be present in free form as esters of fatty acids or as glucosides. Addition of caustic soda is also effective to remove heavy metals such as Fe, Ni, Zn and Sn. They are generally retained in palm soapstock and partly in palm acid oil.

Quality and Composition of Palm Fatty Acid Distillates (PFAD)

Following the development of refining techniques, alkali refining of palm oil is carried out sometimes in the users' countries only, especially when the imported crude oil quality is not at its best or there are some special quality requirements of the finished products. In the producing countries, on the other hand, this practice is restricted to some occasional production of neutralized palm oil (NPO) which is meant to take the economic advantages of the current export duty schemes like those being enforced in Malaysia rather than for purely technical reasons. Practically all fully refined palm oil products are processed by physical or steam refining in Malaysia and Indonesia today. Generally speaking, physical refining has fewer operational steps, less chemical consumption, and more favorable refining factors and thus offers a more attractive overall processing cost. PFAD is a byproduct from the distillative operation of physical refining (see Fig. 2) and to a less extent, deodorization after alkali refining. According to the present trend, we expect the supply of palm acid oil to decrease and be replaced largely by PFAD. The specifications and some typical analytical data of various types of PFAD are given in Table III. The FFA content in PFAD is very much higher than that in palm acid oil, a result confirming relatively less neutral oil losses during refining. The presence of neutral oil in PFAD is mainly due to phase equilibrium of the system as determined by thermodynamics and vapor entrainment. In fact, a good proportion of this neutral oil is mono- and diglycerides. This is because they are more volatile than triglycerides. They may come from the original crude oil or be formed by hydrolysis of crude oil during refining. In trade practice, PFAD is sold on a similar basis as acid oil except there is no need to mention soap content (3,4). As in the case of palm acid oil, PFAD can be used directly for production of low quality laundry soap. Because of its low moisture content, PFAD, unlike soapstock, does not ferment or emulsify readily. Due to its corrosive nature, especially at elevated temperature, aluminium or stainless steel lined vessels may be required for storage or delivery. For prolonged holding, darkening of color and development of unpleasantly pungent odor may occur which may make subsequent treatments difficult.

In addition to FFA and neutral oil, PFAD contains most of the odoriferous substances from crude palm oil. These are mainly high molecular weight ketones. They are present only in traces (less than 0.1% by weight) in the original crude oil. During the transfer of these ketones from oil phase to PFAD, some forms of chemical changes or degradations may have occurred but the nature of which is yet to be identified. Steam refining also decomposes carotenoid compounds, carbohydrate and protein compounds, peroxides and aldehydes in the oil. Except for peroxides and aldehydes, we do expect that most of the other compounds will remain in the oil. On the other hand, a minor proportion of sterols is transferred to PFAD by physical refining. PFAD is a good source of tocopherols and tocotrienols. Up to 3-8% of tocopherols and tocotrienols have been identified in some productions (5). During physical refining, heavy metals are normally trapped by scavenging agents such as citric acid, tartaric acid or phosphoric acid.

Quality and Composition of Spent Bleaching Earth

In addition to palm soapstock, palm acid oil and PFAD chemical and physical refining plants also have spent bleaching earth as byproduct. The quantity ranges from 0.5-2.5% of the weight of oil processed.

Bleaching is a physical absorption process and pigments are irreversibly absorbed onto the clay. It also absorbs traces of soap and heavy metals. The oil retention in spent earth, to a large extent, is related to its activity and particle size. Generally it ranges from 25% to 75% of the spent earth weight. The oil retention is also affected by the type of filters used, the conditions of steam and air blows and the amount of activated carbon present.

The best way to treat spent bleaching earth is by solvent extraction. If proper solvent is selected, the quality of the recovered oil can be comparable to that of the bulk of the bleached stock, especially when special precautions to reduce oxidation have been exercised. Hexane works well. Care must be taken if a strong polar solvent such as acetone or trichloroethylene is chosen. It may remove color pigments and other impurities from the spent earth in addition to the recovered oil. Recovery of oil from spent earth is economically attractive only where large volumes of spent earth are available to be processed. It may be practical to have a central treatment facility in an area where a number of refining plants are located.

There are many other ways to treat spent earth. The water separation may be a cheaper way. In this method, the greatest disadvantage is the disposal of wet clay. This has been discouraged or prohibited in many countries' regulations. Of course, the quality of recovered oil is also inferior. Another way is to install an incinerator to burn the organic substances in the earth for energy production. This treatment is not without problems, because of the large volume of noncombustibles. It may also be used for cattlefeed.

More often than not, spent earth eventually finds its way to a landfill. Again, fire hazard and odor problems must have to be looked at especially when the spent earth

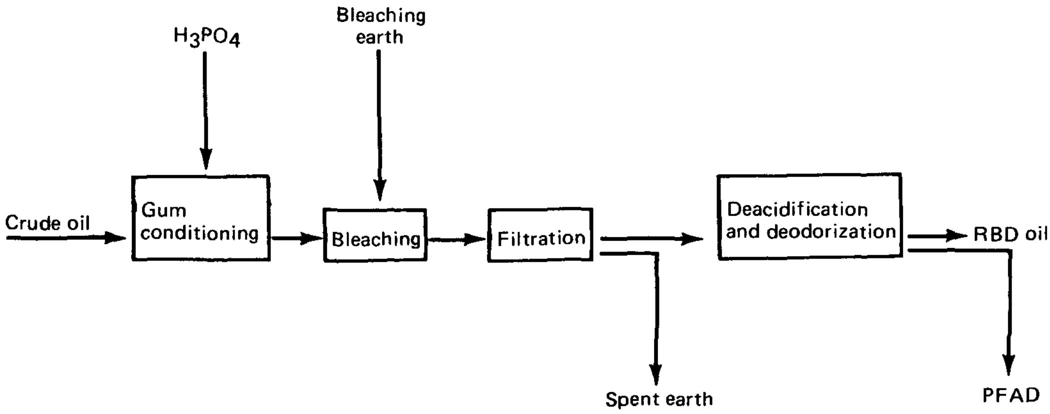

FIG. 2. Steam (physical) refining process.

TABLE III

Typical Specifications of PFAD

	From palm oil	From palm olein	From palm stearin
FFA (%)	85.00-90.00	85.00-90.00	85.00-90.00
TFM (%)	95.00-98.00	95.00-98.00	95.00-98.00
Moisture (%)	0.10- 0.50	0.10- 0.50	0.10- 0.50
Unsaponifiable matters (%)	0.50- 3.00	0.50- 3.00	0.50- 3.00
IV	51.00-55.50	57.50-60.00	36.00-48.00
Titer (C)	37 -44	19 -26	43 -50
GLC Analysis (typical results only)			
C 12:0	0.3	0.9	0.1
C 14:0	1.4	1.6	0.9
C 16:0	47.4	44.9	57.0
C 18:0	4.4	4.0	5.3
C 18:1	36.9	38.1	30.5
C 18:2	8.4	9.2	6.2
C 18:3	0.4	0.6	Tr
C 20:0	0.4	0.4	Tr
C 20:1	0.2	0.3	Tr

has not been treated.

Quality Requirements of Palm Acid Oil and PFAD for Use in Feed and Fatty Acid Manufacture

Feed industry. Although fatty materials were not added to animal feed in any appreciable amount before 1954, they are one of the essential components today. They are high energy feeds which give 9 cal/g when metabolized as compared to 4 cal/g in the cases of starch or protein. They can also act as carriers and protectors for several fat-soluble vitamins and antioxidants. Nevertheless, before they can be used in animal feeds, they have to compete with some cheaper nonfat energy sources such as corn which gives 3.5 cal/g. Therefore, fatty materials price must at least be less than 2.6 times corn price before they are economically competitive for use in animal feeds.

On the other hand, according to the Morrison digestibility table, fatty materials can be 95% digested, whereas corn can only be 85% digested. With the development of effective but inexpensive antioxidants, the stability of fatty materials against oxidation is also ensured. As a result, some low grade fats have found their way into the feed industry.

Some common specifications of fatty materials used for animal feed are given in Table IV (6). Traditionally, low grade tallow and grease have been used. From the table, we can conclude that acid oil and PFAD from most of the palm oil products can also be used. There may be some inherent problems associated with these products. For instance, any residual sulfuric acid and its reaction products (sulfates and sulfonates) in palm acid oil decreases palatability to most animals. Furthermore, the presence of pesticides in PFAD may also restrict its usages. Due to

TABLE IV

Specifications of Fatty Materials Used in Animal Feed

Quality item	Specifications
FFA	ca. 15.0%
Moisture	0.5%-2.0%
Impurities	Traces
Unsaponifiable matters	3.0% maximum
Titer	44 C maximum
Peroxide value	15-20 maximum
AOM stability	ca. 20 hr
Color	Light

relatively high FFA content, it may be advisable to mix them with some other fats before blending into feed. This is done more for good palatability than for technical or nutritive reasons.

Fatty acid industry. Fatty acids are usually derived from natural oils and fats (7). As a result, fatty acid industry does become a natural outlet for palm acid oil and PFAD.

Oleochemicals from fatty acids have found applications in food, paper, plastics, rubber, lubricants, soap, cosmetics, toiletries, surfactants, pharmaceuticals, fertilizers, textiles, etc. Figure 3 indicates some of the processes to convert fats such as acid oils and PFAD into basic oleochemicals which may serve as starting raw materials for industries mentioned above (8).

For both palm acid oil and PFAD, pretreatment with sulfuric acid is generally not needed, unless soap content in acid oil is so high (say, above 0.1%) that it may cause emulsification during fat splitting. In some cases where neutral oil content in PFAD is not high, the fat splitting process may also be omitted. This will, of course, increase the volume of pitch during straight run distillation. Distilled fatty acids can be used as starting materials for surfactants and surface coatings, but a large proportion of them has been used to make good quality household and industrial soaps. Traditionally, toilet and cosmetic soaps have been made from a fat charge consisting of tallow and coconut oil in order to obtain an optimum balance between lathering and solubility. Tallow production has remained static for recent years. From a comparison of fatty acid composition, it seems that distilled fatty acids from palm acid oil and PFAD can offer an alternative route to make toilet and cosmetic soaps.

Apart from soap making, distilled fatty acids from palm acid oil and PFAD can also be further treated in some of the following ways: e.g., by catalytic hydrogenation to produce 'stearic acid'. This is, of course, not pure stearic acid in the technical sense, but a mixture of many saturated acids with IV normally ranging between 0.5 and 8.0. Typical applications have been found in rubber, plastics, candle, lubrication, emulsifier as well as some food and

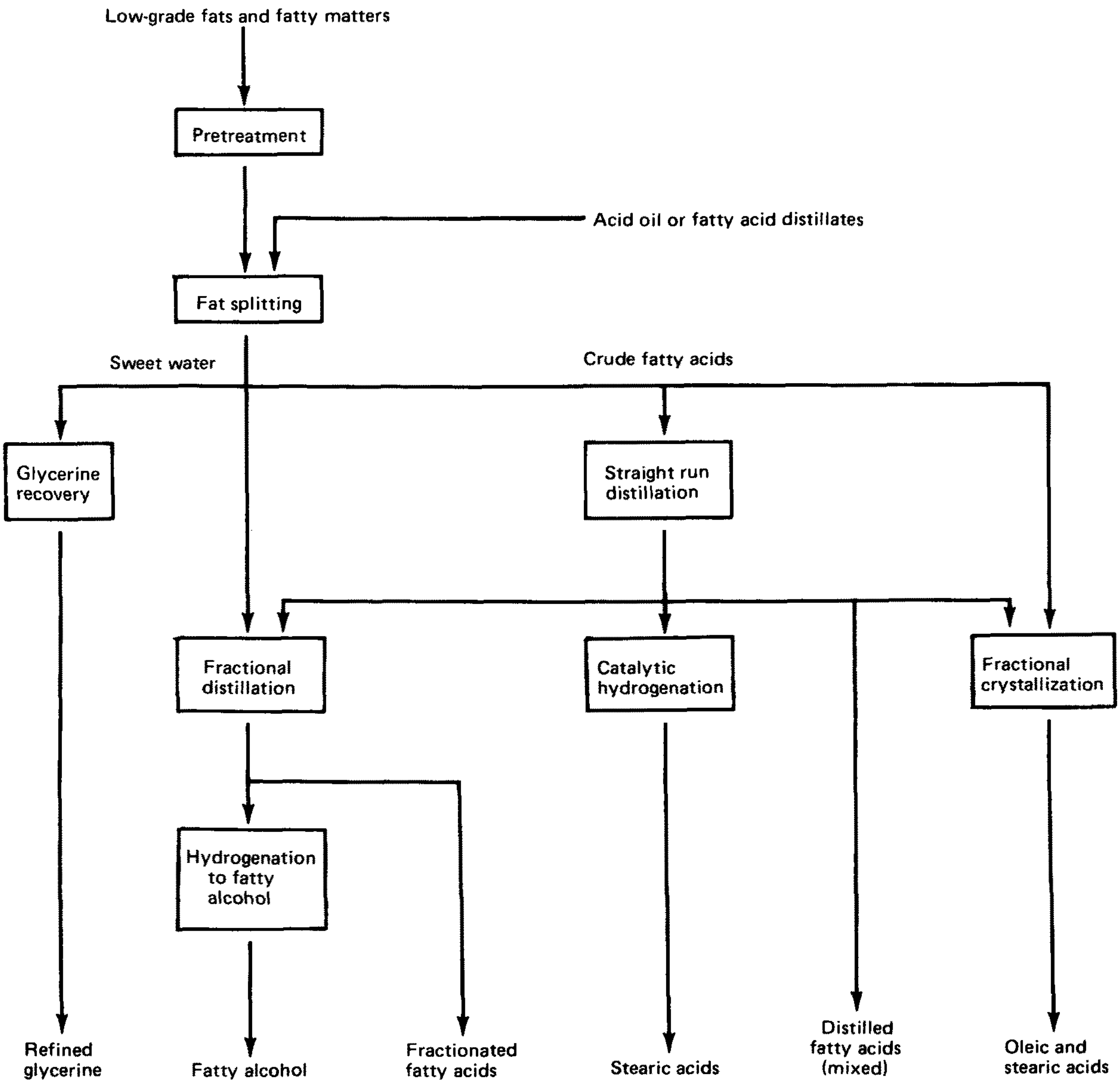

FIG. 3. Processes for conversion of fats into basic oleochemicals.

pharmaceutical preparations.

Secondly, they can be subjected to fractional distillation to produce fractionated fatty acids. These are used in cosmetics, food emulsions, polymerization initiators and fatty alcohols.

Thirdly, they can be subjected to fractional crystallization. This is carried out by using a wetting agent which transforms fat crystals into an aqueous suspension followed by centrifugal separation from liquid phase. As in the case of palm oil fractionation, the crystalline phase is normally known as 'stearin' and the liquid phase as 'olein'. While stearin can be converted into stearic acid by slight or no hydrogenation, olein has found applications in liquid soap, textile, lubrication and leather industries.

In processing palm acid oil and PFAD, many problems call for attention. The first one is the development of unpleasant odors during prolonged storing and/or heating. These may have something to do with the odoriferous substances (ketones) originally present in the crude oils. But the actual mechanism is yet to be investigated. Another problem is the darkening of color. Lurgi has found that color stability can be improved by proper pretreatments, heavy ends removal and hydrogenation (9). Lim et al. have attributed discoloration partially to oxidation and partially to the presence of minor components (10). On the other hand, Krygier et al. found that heat decolorization is a result of formation of oligomers due to heating (11). Deterioration of color and odor of palm acid oil and PFAD directly affects the quality of finished products. In many incidences, they have practically prevented palm acid oil and PFAD from further applications. Some of the unsaponifiable matters have also created difficulties during distillation. Their presence in distilled fatty acids has not only reduced the purity of these oleochemicals, but also affected directly or indirectly the quality of subsequent products.

BYPRODUCTS FROM REFINING OF OTHER OILS

Other oils and fats are mostly alkali refined. Nevertheless, such practices may change in future, as some achievements in applying physical refining to other oils have been reported in recent literature (12). On the other hand, it is also certain that some heat sensitive oils, such as cottonseed oil, will not be able to accommodate high temperature treatment without alkaline neutralization.

The quality and composition of soapstock from these other oils, like palm oil, depend on the type of processing equipment, the concentration and type of neutralizing agents, the operating conditions, the quality and grade of feedstocks and finished products. In general, continuous refining plants offer better refining factors than batch (kettle) refining plants because less oil losses in saponification, entrainment and emulsification. A difference of oil losses up to 20-30% is not uncommon in practice. This will lead to higher FFA content in soapstock and acid oil from continuous refining plants. In terms of oil nature, soapstock from refining of high acid oils will have less neutral oil content than that of low acid oils. This may be due to less opportunity for oversaponification. But great difficulty of separation may be encountered if FFA of crude oil is too high (say, 8-20%). In this case, high losses due to emulsification and entrainment may occur. On the other hand, soapstock and acid oil from lauric oil refining will have higher FFA content. This may be attributed to shorter chain length and less phosphatides. Degumming prior to refining normally offers some improvements of FFA content in soapstock and acid oil. There are claims that gossypol in cottonseed oil possesses beneficial properties on oil losses in alkali refining. But it is not reflected in the quality of its soapstock. In addition to dosage and concentration of neutralizing agents, other factors such as mode of addition, contacting time, degree of mixing, neutralizing temperature, etc., have also important bearings on the final quality and composition of the soapstock and acid oil.

As in the case of palm oil, those impurities originally found in crude oils such as phosphatides, carbohydrates, proteins, pigments, sterols, heavy metals, etc., are transferred in part or full to soapstock and acid oil during refining. Gossypol and related pigments in cottonseed oil are almost completely removed to soapstock.

From the product usage viewpoint, with the exception of lauric oils, soapstock from other oils is not expected to be used directly for soap making. This is because of their high unsaturation, low titer and high color. But they may be able to do so after some form of hydrogenation. In fact, claims have been made for using soapstock from sunflower and safflower oils for soap making (13). Nevertheless, these soapstocks and acid oils constitute good starting materials for feed and oleochemical industries.

The treatments of spent earth from palm oil refining can be equally applied to that of other oils. The quantity normally ranges between 0.5% and 4.0% of the processed oil weight. Special care must be exercised to prevent fire hazard and oxidation of oil prior to and during recovery. This is particularly true for the highly unsaturated oils. Commercial lecithin is recovered by degumming soybean oil. This is normally conducted in the oil extraction plant rather than in the refinery stage. Other vegetable oils, such as corn oil, sunflower seed oil and peanut oil can also yield gums suitable for conversion to lecithin. But such recovery is seldom carried out in commercial scale.

REFERENCES

1. Alfa-Laval, Technical Bulletin on Halvopon Or Process.
2. Cavanagh, G.C., JAOCS 53:361 (1976).
3. National Cottonseed Products Association, Rules Governing Transactions Between Members, Memphis, TN, 1961.
4. National Soy Bean Processors Association, Year Book and Trading Rules, Chicago, IL, 1961.
5. Gopor, A.B., et al., Proceedings of Palm Oil Product Technology in the Eighties, Kuala Lumpur, 1980.
6. Galf, J.A., Technology of the Use of Fats in Feeds, NRA.
7. Schwitzer, M.K., manuscript (1981).
8. Johnson, D.H., JAOCS 55:438 (1978).
9. Lurgi Express Information on Fatty Acid Technology, T1167/1-78.
10. Lin, S.S., A.L. Hsieh, D.B.S. Min and S.S. Chang, JAOCS 53:157 (1976).
11. Krygier, K., J. Brzezniski and A. Rutkowski, Riv. Ital. Sostanze Grasse LVII:424 (1980).
12. Sullivan, F.E., Proceedings of the Malaysian Palm Oil Conference, Kuala Lumpur, 1978.
13. Sonntag, N.O.V., JAOCS 58:155A (1981).