TABLE VII
Summary of Mol % Dibasic Acid Recovery

Acid oxidized	C_{13}	C_{12}	C_{11}	C_{10}	C_9	C_8	Total
9,10-Dihydroxystearic	—	—	—	2.0	95.3	—	97.3
Oleic (A)	—	—	—	—	89.9	1.6	91.5
Oleic (B)	—	—	—	1.4	90.5	—	91.9
Oleic (C)	—	—	—	—	90.5	1.2	91.7
Elaidic	—	—	—	—	94.7	0.9	95.6
10-Undecenoic	—	—	—	86.2	2.1	0.8	89.1
Erucic	83.2	2.5	—	—	—	—	85.7
Vaccenic	13.5	27.6	21.0	5.2	—	—	67.3
Azelaic	—	—	—	—	98.8	—	98.8
Azelaic + pelargonic	—	—	—	—	98.8	—	98.8

Erucic acid (13-docosenoic), also from Eastman Kodak Company (No. 2233 Red Label), after recrystallization from 30% ethanol and oxidation showed total dibasic yield (Table VI) of 85.7% with a minor amount of unsaturation at the C_{12} position.

Vaccenic acid (11-octadecenoic) supplied by Jasonols Chemical Corporation, Brooklyn, N. Y., after recrystallization from acetone at —60°C. on oxidation (Table VI) gave 13.5% brassylic acid, 27.6% dodecadianoic acid, 21.0% nonane dianoic acid, and 5.2% sebacic acid. Thus the "pure" acid after recrystallization contained a minimum of 21% and a maximum of about 31% vaccenic acid.

Oxidation of 9,10-dihydroxystearic acid was conducted as a control on handling and processing technique as previously mentioned. King (9) and Robinson (13) have reported quantitative yield of 9,10-dihydroxystearic acid by potassium permanganate oxidation of sodium oleate. Our tests with variable ratios of periodate and permanganate gave uniform yields of dibasic acids. Total dibasic recovery of 97.3% was considered good evidence that our technique was practically quantitative and that it was not the cause of the lower yields established for oleic acid. The method could be used to establish the purity of similar isomeric compounds.

The special control tests designed to determine the effect of oxidation and handling on the end-products formed from oleic acid have shown practically quantitative recovery. These tests were crucial. Data for oxidation of a chromatographically pure sample of azelaic acid on three occasions (Table II) not only show good agreement but practically quantitative recovery. A single oxidation of a mixture of azelaic acid and pelargonic acid has also shown practically complete recovery of the dibasic acid. Consideration of these control tests and the oxidation of 9,10-dihydroxystearic acid permits us to conclude that the method as disclosed was practically quantitative but that yields for oleic acid were diminished because of some unknown factor during oxidation *per se*. All data are summarized in Table VII.

Conclusions

Periodate-permanganate oxidation of three samples of oleic acid considered to be of high purity has given reproducible but less than theoretical amounts of total dibasic acids. Recovery approximated 92% with about 90.3% of the expected azelaic acid. Recovery of other dibasic acids indicated that about 1.5% of the total unsaturation of these samples of oleic acid was present in positions 8 or 10 in the fatty acid molecule.

Oxidation of elaidic acid produced from one of the oleic acids has given total dibasic acid yield of about 96%, with a smaller amount of its total unsaturation in the same position as in the parent oleic acid.

Oxidation of high purity 9,10-dihydroxystearic acid has given essentially quantitative yield of total dibasic acids. The method described should be useful in determining the composition of similar unsaturated positional isomers.

Controls showing the effect of the method on azelaic acid and on a mixture of azelaic acid with pelargonic have shown essentially quantitative recovery of azelaic acid. Failure to establish quantitative recovery on oxidation of oleic acid must be caused by some unknown factor during oxidation *per se*. The experimental technique described was satisfactory for quantitative studies of the type undertaken.

Oxidation of moderate-purity, mono-unsaturated fatty acids, such as erucic, 10-undecenoic, and vaccenic acid, has given mixed dibasic acids corresponding to the respective positions of unsaturation.

The data indicate that the method described shows the position of minor unsaturation within about 1%.

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The Refining and Bleaching of Vegetable Oils

EDWARD M. JAMES, Consultant, Swarthmore, Pennsylvania

A DISCUSSION of refining and bleaching of vegetable oils, as a section of this symposium on unit processes, must, of necessity, be in the nature of a review of those methods which are now in use or available to the manufacturer. Most, if not all, of these methods have been made the subject of numerous papers which have been presented before the American Oil Chemists' Society over the last 25 years and are available to the student who wishes full details in the files of the Journal, and elsewhere.

Some of the most important have been covered by basic patents which have expired or which have only a relatively short period to run. It would seem best to treat the subjects of refining and bleaching separately; and, since refining is usually carried out before bleaching, this process will be covered first.

Definition and Object of Refining

The term "refining," as understood in this country, refers to the removal of certain minor constituents from crude fats and oils, with as high a yield as possible of purified glycerides. The minor constituents which are to be removed are gross dirt and moisture, non-fatty materials which are loosely termed "gums" or phosphatides, color bodies or pigments, and, in most cases, free fatty acid.

Gross dirt and moisture can be removed either by settling or by filtration. The phosphatides of crude oils can be divided into two classes: those which can be coagulated and rendered insoluble in the oil by treatment with water, and those which are noncoagulable by water. The percentage of the former is considerably higher than of the latter.

Fundamentally the refining process is the most important to which vegetable oils are subjected before being converted to finished products. If the oil is not properly refined, subsequent steps such as bleaching, hydrogenation, winterizing, deodorization, etc., will not proceed smoothly and the final product will not be up to quality standard. If refining is inefficient and the highest possible yield of properly refined oil is not obtained, this inefficiency is reflected in lowered yields of finished products, and the profit of the manufacturer is reduced. Oil lost in the refinery cannot be recovered. The manager of finished products of a large manufacturer of edible oils once stated: "after all, we make our money in the refinery. No matter how efficient our subsequent process steps may be, the amount and quality of the material leaving our plants in the finished packages depends upon how well our refiner has done his job."

For certain industrial uses some oils, notably soybean oil and linseed oil, can be sufficiently purified by a refining process known as degumming. Oils thus treated still contain small proportions of phosphatides, color bodies or pigments, and free fatty acids.

Substantially complete removal of all the minor constituents of fats and oils may be accomplished by treating the crude oil with relatively strong solutions (12°–20° Baumé) of caustic alkalis, usually caustic soda. The alkali neutralizes the free fatty acids, and in part, decomposes the phosphatides. The amount of color bodies or pigments in the refined oil is greatly reduced.

If a crude oil is treated with the exact amount of caustic solution required to neutralize the free fatty acids as determined by the official methods of the A.O.C.S., the final product will not be a neutral oil but will titrate to 0.15% or more F.F.A., depending upon the initial free fatty acid content and the amount of phosphatides present originally in the crude. Further, practically all the original color bodies still remain in the oil. It is thus obvious that the chemical reactions involved overlap, *i.e.*, before substantially complete neutralization of the free fatty acid has taken place, the caustic has begun to decompose the phosphatides. These materials are far more readily saponified than neutral triglyceride; indeed they will absorb some of the very dilute caustic solution used in the standard method for the determination of free fatty acid, and the test is therefore not a measure of the true free fatty acid present in the crude unless it is completely free of phosphatidic materials.

As an example, the writer had the opportunity some years ago, to study samples of cottonseed and soybean oils which had been decolorized by liquid-liquid extraction with propane. The decolorized oils had been completely freed of minor impurities, except free fatty acids and a small amount of color bodies.

The untreated soybean oils varied in free fatty acid content, as determined by the standard A.O.C.S. method, from 0.5%–0.7%. The depropanized overheads showed an average of less than 0.35% F.F.A. when analyzed by the same test. The cottonseed oils gave a slightly lesser drop in acid (0.2%–0.3%), but the trend was the same (1).

In order completely to refine a crude oil and remove the bulk of the color bodies, together with the phosphatides which are incoagulable by water, it is necessary to use a certain excess of caustic over that required by the free fatty acid. The role of this excess caustic in absorbing color is obscure and has been the subject of much theoretical discussion based on meager experimental evidence. It has been stated that color removal is effected by adsorption of the color bodies in the soap present in the refining mixture, that not only is soap required but there must be some saponification of neutral oil for such adsorption to take place.

If this is the whole story, it should be possible to obtain very light refined oils at the expense of yield by the use of extremely high excesses of caustic solution in the refining operation. In practice, this is not true since there seems to be an irreducible minimum in color for each individual oil, and, beyond the point at which this is achieved, increased excesses of caustic solution merely serve to reduce the yield of refined oil.

Another theory which has been advanced is that the color bodies in a crude oil are soluble in caustic solution and that this solubilization is the reason that excess caustic is required. Some support for this theory is afforded by the European manner of refining certain dark cotton oils, particularly Egyptian crudes, which is to treat with a relatively small amount of caustic soda solution to remove substantially all the free fatty acids and nonfat and, after settling out the soapstock, to give the partially refined oil a number of washes with very dilute caustic solution, separating the dark-colored aqueous layer after each wash and thus successively reducing the color of the oil until it meets the standard desired. Losses in these so-called "color washes" are extremely low and may amount to as little as 0.2%–0.3% per wash, with the result that the multiple treatment will give a lighter oil than can be obtained with a heavy treat in the first stage, with a higher yield.

In refining there is some saponification of neutral oil by the excess caustic either in refining or in color washing as described above, but whether the color removal results from the solubility of color bodies in the caustic solution or from adsorption in the soap, or from a combination of both, remains to be proven and might well form the basis of a fundamental research project.

In refining, of the main chemical reactions involved, *i.e.* neutralization, coagulation, and decomposition of phosphatides, removal of color bodies, and saponification of neutral oil, the first two are much more rapid than the last, and this fact has been taken advantage of in modern methods of continuous refining.

There is also the question as to where and when the major part of saponification occurs in the refining process. Before the soap particles, or foots, can be effectively separated from the refined oil, they must have coagulated to a certain degree. In the old kettle type of refining, this coagulation required long stirring and heating. As the foots, or soapstock, agglomerated, they entrained a considerable amount of neutral oil. After settling out and standing for a few hours, the layer of soapstock beneath the refined oil, although it contained a considerable quantity of neutral oil, was found to be slightly acid despite the excess of caustic which had been used in the refining.

On the other hand, the soapstock which is separated rapidly and continuously from the refining mixture by centrifugal force and in cases where the span of time between mixing of the crude with caustic and the substantially complete separation of refined oil and soapstock may be as little as two minutes or less, if analyzed as soon as it is discharged from the separator, will show a much higher neutral oil content than if it is allowed to stand for some hours. This indicates that at least a considerable proportion of the saponification occurring in refining takes place in the neutral oil which is entrained in the particles of soapstock.

Crude oils vary considerably in the type and quantity of the minor constituents present, depending upon their sources. The principal stocks commercially refined in this country, arranged in order of the tonnage available, are soybean, cottonseed, linseed, corn, coconut, and peanut.

Soybean oil is usually relatively low in free fatty acid and contains a considerable amount of phosphatides unless it has been degummed. Certain soybean oil producers make a practice of degumming at least an appreciable portion of their production of crude oil in order to use the separated gums in the manufacture of soybean lecithin. Cottonseed oil is usually higher in free fatty acid than soybean, and the acid is spread over a much wider range. Phosphatide content is generally lower. The color of crude cottonseed oil is generally darker than that of crude soybean oil, but color removal in refining is considerably greater. The free fatty acid in crude corn oil is similar in amount to that found in crude cottonseed oil, but the phosphatide content is lower. Crude colors are usually lighter than with cottonseed oil, but color removal in refining is not so great. The free fatty acid of good grade crude coconut oil varies between 3.0% and 5.0%; it contains almost no phosphatides, and its color is very light. Color removal in refining is excellent. Good crude peanut oil has a fatty acid range slightly lower than that of crude cottonseed; it contains very little gums and coloring matter and, when refined, produces a very light oil. Crude linseed oil, in general, has a slightly higher free fatty acid than soybean oil; its gum content is lower, and the color of the refined oil is usually darker than that of soybean oil.

Degumming

The two oils most commonly degummed in this country are soybean oil and linseed oil. The degumming of soybean oil is, in reality, two distinct processes.

The first is for the recovery of lecithin. For this purpose it is desirable to obtain a sludge, or coagulated gum, having as high an acetone-insoluble content as possible, as well as a low moisture. No attempt is made to obtain a totally degummed oil.

The water used in degumming is brought into contact with the oil by mechanical agitation in a holding, or steep, tank at a temperature of 130°–160°F. Agitation is usually continued for approximately 30 min. in order to allow the gums to coagulate, and the contents of the tank are then passed through a centrifugal separator in which the mixture of oil and gums is separated continuously into sludge and degummed oil. The moisture in the gums depends upon the amount of water originally added. All the water however is not absorbed in the gums, but some of it remains in the degummed oil. The latter is passed continuously through a vacuum dryer and goes to degummed oil storage. The gums are sent to the lecithin recovery plant, where they are dehydrated and processed into various grades of commercial lecithin.

Since gums of low moisture content are desired for lecithin manufacture, the amount of degumming water is held down to a level of between 1.0% and 2.0%. It is desirable to have as high a percentage as possible of acetone insolubles in the gums in order to minimize the loss of glyceride. A part of the glyceride contained in the gums is probably in solution, but a part is also entrained. Under proper conditions of centrifugation it is possible to increase the acetone insoluble of the gums to upwards of 70.0%.

The degummed oil from the above operation may or may not be heat-break free. It is usually sold as degummed crude under Rule 102 of the N.S.P.A.

In addition to the process described above, in which the water is added in a steep tank to the crude oil, there are several other methods in use. The water may be proportioned continuously into a stream of oil, then mixed in a mechanical mixer, passed continuously through a heater in which the temperature is raised to the desired point, and then separated centrifugally. Another method is to treat the oil continuously with a required percentage of water in the form of steam, which insures an intimate contact with the dissolved gums. In this case however it is necessary to agitate the mixture of condensed steam and crude oil to allow time for coagulation, followed by heating to the desired temperature before centrifugation.

If it is desired to make as completely degummed an oil as possible, one which will be heat-break free and can be used for industrial purposes, larger amounts of steam or water for coagulation of the gums are used, and the capacity at which centrifugal separation is carried out is somewhat lowered.

Recently a novel process for the complete degumming of soybean oil has been described and patented (2). In this process the crude soybean oil is intimately mixed with a small amount of acetic anhydride, the proper amount of water to hydrate the gums is added, and, after a short tempering and heating time, the hydrated gums are centrifugally separated. The degummed oil is then continually washed with water to remove traces of acetic acid and is continuously vacuum-dried. It is said that soybean oil degummed in this manner is completely break-free and can be bleached and deodorized without caustic refining to produce a stable product.

Break-free degummed soybean oils are usually sold under N.S.P.A. Rule 103 at a fixed premium over crude plus freight, Decatur basis.

In the degumming of linseed oil the objective is to obtain as complete freedom from heat break as possible, together with a low A.S.T.M. foots test. The separated gums have no value as lecithin and are usually acidulated and sold as acid oil. The percentage of water used in linseed oil degumming varies from 3.0%–5.0%, and the separated gums, although low in acetone-soluble content, are quite wet. Sometimes, instead of being acidulated, the linseed gums are returned to the meal, where they serve to raise the fat content.

Degumming of both soybean and linseed oil is almost invariably carried out at the crushing plant since the mill has the best opportunity for utilizing the gums.

The degumming of cottonseed oil has been studied on a laboratory and pilot plant scale for many years; but, so far as we are aware, has been employed commercially by only one producer. In this case the separated gums are added to the meal from the solvent-extraction plant and serve not only to increase the fat content of the latter and prevent dusting but to improve the operation of making the meal into pellets.

Refining

For many years refining was carried out in the open kettle. This was usually a cylindrical tank having a steep, cone bottom; it was equipped with steam coils, a variable-speed agitator, and swinging suction lines for withdrawing the refined oil from the surface of the soapstock. Refining kettles varied in capacity from 20,000 to 120,000 lbs. of crude oil.

Kettle refining was an art, and many refiners developed a high degree of skill in obtaining high yields and refined oil of good quality (3).

Although in recent years the old refining kettle has been largely replaced by continuous refining equipment, employing centriugal separators to separate refined oil and soapstock, it is still used for certain refining operations. The most important of these is the refining of coconut oil, in which kettle technique has been carried to such a point that the continuous process cannot improve yields materially. Refining kettles are also widely used for the re-refining of cotton oil to obtain improved colors, and in recent years a highly successful process for the kettle refining of degummed soybean oils, in which the refining is carried out in the presence of complex, polyphosphates, such as tetrasodium phrophosphate, has been developed and is in use in several large refineries in this country (4).

Twenty-five years ago, when the first continuous refinery was installed in this country, the principal vegetable oil refined was cottonseed. Even when this oil was refined by the best kettle technique available, the refining ratio (loss divided by free fatty acid of the crude) was high. Soapstock from refining in the open kettle contained 25%–30% of neutral oil. The spread in value between refined cottonseed oil and soapstock was high, and it appeared that any process which would increase the yield of the former would be commercially attractive.

The first continuous refining process, which has now become known as conventional caustic refining, is a relatively simple operation (5). A continuous stream of crude oil at a temperature of 70°–90°F. is mixed continuously in a mechanical mixer with a proportioned stream of caustic soda solution. The percentage and strength of the caustic solution depend upon the characteristics of the original crude and the bleach color desired in the final refined oil. From the mixer the stream of caustic and oil is passed through a continuous heater, where the temperature is raised to 130°–160°F. and thence flows to a battery of continuous centrifugal separators, where the refined oil and soapstock are separated. The refined oil is washed once or twice with hot water continuously; the soap water is separated in another battery of continuous centrifugal separators; and the refined oil, which contains a small amount of moisture, is dried continuously in a vacuum dryer.

When working with cotton oil, plant-scale tests made by the kettle process and the continuous process on identical lots of oil showed an improvement in loss of 25%–30% in favor of the continuous process to produce oil of comparable bleach colors and quality.

These results led to the general adoption of the Conventional Caustic Process, and today it is still more widely used than any other.

Since there is no longer an opportunity to compare the results of the continuous process with kettle operation, it has become the custom, in many refineries, to use the settlement loss as determined by the standard A.O.C.S. refining methods as a standard of comparison with the continuous process. Over the years mill operation has improved considerably, and settlement losses are now materially lower than they were 25 years ago. As a result of this change in standards of comparison, loss improvement realized by the continuous conventional caustic process has, in many cases, been reduced to 15%–20%.

The Conventional Caustic Process is the simplest of all continuous refining methods. When properly operated with due care to the maintenance of the equipment, it will give consistent results. It requires reasonable supervision and careful lye selection for the different types of oil by an experienced superintendent.

Some years subsequent to the development of the continuous caustic refining process, another refining method, known as the Full Soda Ash Process, was developed (6). This is a two-stage refining method in which the free fatty acids of the crude oil and the phosphatides are neutralized and coagulated by a nonsaponifying alkali, such as soda ash. After separation of the soap and phosphatides in the continuous centrifugal separators the partially refined oil, which is rather dark in color, is continuously treated with a small percentage of strong caustic soda to reduce the bleach color to the desired level.

The Full Soda Ash Process is operated as follows. A continuous stream of crude oil, heated to approximately 140°F. is mixed with a sufficient quantity of strong soda ash solution proportioned into the stream to neutralize the free fatty acids. Sufficient excess is usually employed to convert the carbonate to bicarbonate, rather than to CO_2 and water. The mixture is then heated to approximately 200°F. and passed through a dehydrating tank, maintained under vacuum, in which the soapstock and coagulated gums are dehydrated to a substantial degree and free carbon dioxide is removed. From the dehydrating tank the mixture of oil and partially dehydrated soapstock is rehydrated by means of a proportioned stream of strong sodium carbonate solution, and the mixture is then passed continuously through a battery of continuous centrifugal separators in which the oil and soapstock are separated. The dark-colored, partially refined oil is accumulated in a small surge tank, from which it passes through a cooler, where its temperature is reduced to 100°F. or less. The cool oil is mixed continuously with a small proportion of strong caustic soda solution (20°–30° Baumé) to remove the coloring matter as far as possible, heated to approximately 160°F. and continuously separated into refined oil and dark lye in a second battery of centrifugal separators. These re-refining machines are equipped with a water flush in the bowl, which allows free discharge of the mixture of heavy soap and lye formed by the re-refining treat. The refined oil from the re-refining centrifuges is washed, either once or twice with water as in the Conventional Caustic Process, vacuum-dried continuously, and sent to storage.

The advantages of the Full Soda Ash Process lay in the fact that there was no saponification of neutral oil in the primary treat with soda ash, and losses of the former were limited to small amounts entrained in the soapstock. Since the time of contact between the partially refined oil and the strong caustic in the second step is very short, saponification is held to a minimum. There is no danger of oil loss through over-treating with soda ash in the first step, hence the proportioning equipment at this stage is relatively simple. Somewhat less careful supervision is required for the successful operation of the Full Soda Ash Process since, in the first stage, the soda ash solution used is dependent only upon the free fatty acid, and in many oils a fixed percentage of strong caustic in the re-refining step is satisfactory.

On the other hand, the Soda Ash Process is more complicated than Conventional Caustic and requires a considerably larger amount of equipment. Steam and water usage is relatively high on account of the double vacuum system necessary and the requirement for cooling the partially refined oil. In addition, with a good many cotton oils it is difficult to match the best bleach color possible when the oil is refined in the laboratory according to the standard A.O.C.S. refining test. The carbonate foots are low in total fatty acid and have to be acidulated before they can be sold. There are many problems in acidulation and acid usage is high on account of the necessity for neutralizing the sodium carbonate.

Nevertheless the higher yields of refined oil, particularly with cottonseed oil, made this process attractive and a number of installations was made.

Recently the Full Soda Ash Process has been modified by elimination of the dehydration and rehydration steps (7). The crude oil is neutralized by the addition of approximately 2.5 times the theoretical amount of soda ash solution required by the free fatty acid and the soapstock and coagulated gums separated in the primary centrifugals. It has been found however that it is necessary to introduce a degassing tank for release of carbon dioxide between the heater and the primary centrifugals. The balance of the process, including re-refining and washing, is precisely similar to that described for the Full Soda Ash Process.

This modified process is particularly suited for cottonseed oils which contain up to 3.0% of free fatty acid. It has the important advantages over the Full Soda Ash Process in that the TFA of the primary soapstock is quite high (35%–40%) and it can be sold without acidulation. The finished oil, after the re-refining stage, is almost invariably equal to or slightly better than, in bleach color, the laboratory bleach on the settlement sample. With dark oils having a settlement bleach of 4 red or higher, the finished refined oil may be more than .5 red lighter than settlement. In cases where the laboratory bleach on the settlement sample is slightly higher than bleachable, it is possible to up-grade these oils from PSY to BPSY.

The foots from the primary separation, which contain soap and undecomposed phosphatides, can be blended with animal feed in order to increase the fat in the ration. Extensive feeding tests with cattle have been undertaken, and the results have been highly promising. Thus a new market may be opened for carbonate soapstock which will not require acidulation.

The Modified Soda Ash Process still has the disadvantage of more complicated and extensive equipment than that required in conventional continuous caustic refining. The limited range in free fatty acid to which the Modified Soda Ash Process is restricted is a further disadvantage. With free fatty acids above 3.0% the volume of soda ash solution required in the neutralization step is excessive. Experimental work on a plant scale is said now to be under way to minimize this difficulty by using a mixture of caustic soda and soda ash solution in the neutralization step, but at present writing this process has not yet been released.

Two other two-step refining processes, which are employed overseas, should also be mentioned briefly.

In the first process, known as the Low Loss Process, the crude oil is conditioned by admixture with 0.1% of citric, or orthophosphoric acid. The mixture is then continuously heated to a temperature of 150°F., and just enough caustic soda solution is added to neutralize the free fatty acid. The mixture of coagulated gums and soaps is then continuously separated in a centrifugal separator. The balance of the process is as described under Modified Soda Ash.

In the second process, known as the Quick Mix Process, the oil to be refined is first continuously degummed, separating the gums in a centrifugal separator, and then continuously mixed with a proportioned stream of caustic soda solution. Time of contact between oil and lye is reduced to a few seconds, and the soapstock is immediately separated in another battery of continuous centrifugal separators. Washing and drying of the refined oil follow along conventional lines.

Another very interesting process of refining, which must be carried out at the crude mills in order to realize its full potentialities, is known as miscella refining. In this country miscella refining has been applied only to cottonseed oil, either in a prepress solvent or whole-solvent mill. In its essentials miscella refining is a simple process. Miscella from the extraction plant is mixed with sufficient caustic soda solution to neutralize the free fatty acids, coagulate the phosphatides, and remove the bulk of the coloring matter. The mixture is then passed through a high-speed centrifugal separator, in which the soapstock is separated from the refined miscella; the latter is then washed with water to remove traces of soapstock and the water separated again in a second battery of separators. The washed refined miscella is then stripped of hexane solvent to give a neutral yellow oil (8).

However the process is not as simple as it appears. Considerable difficulty is encountered in obtaining efficient contact between the caustic soda solution and the miscella. Although sufficient contact between caustic and free fatty acid, to allow the neutralization of the latter, is easily attained, full coagulation of the phosphatides and absorption of the coloring matter do not occur in the course of ordinary mixing, such as is satisfactory for straight crude oil and lye. To obtain complete refining and decolorization of the dissolved oil, two methods have been successfully employed. The first is the use of an homogenizer similar to those used in the homogenization of milk (9), and the second is the addition of small amounts of surface-active agents of the nonionic type to the lye (10). Both methods are covered by issued patents.

Further it has been found that neutralization and decolorization are most effective when the miscella concentration is in the neighborhood of 50% by weight of oil. In a whole-solvent plant this means that removal of the solvent must take place in two stages, a preliminary concentration to approximately 50% oil, followed by refining and washing, and a final removal of solvent. In a prepress solvent plant the intermediate stripping step can be avoided by mixing the crude oil from the expellers with the 20% miscella from the extractor.

Miscella refining presents a number of advantages. Effective removal of free fatty acid and decolorization of the oil can be achieved by the use of quite dilute caustic soda solutions (10°–14° Baumé). The wide specific gravity diffferential between lye and oil hexane solutions greatly increases the efficiency of the centrifugal separation, and it is possible to operate the separators at 50% above their rated capacity in terms of refined oil produced. The soapstock is extremely low in neutral oil. Finally the bleach color of the miscella-refined oil is considerably superior to that which can be obtained by any other type of caustic refining and can be varied by increasing the percentage of refining caustic without serious losses in saponification.

The soapstock from the primary centrifuges contains approximately 17% of hexane; and, in cases where surface-active agents are not used, can be mixed with the meal in the desolventizing equipment to recover the solvent. At the same time the soapstock is spread over the meal uniformly and serves to increase its content of fat.

There are some drawbacks to miscella refining. All equipment used must be totally enclosed and explosion-proof. It must be carefully maintained to prevent excessive loss of solvent during the refining stage. Miscella refining must be carried out at the crushing mills to be effective and economical, and those mills using it must have an outlet for BPSY instead of crude. In our opinion however the high yields of refined oil obtainable and its excellent quality should more than offset these disadvantages.

All the foregoing methods of refining have been proved in commercial operation and are applicable to all the major vegetable oils refined in this country. In order to compare them for efficiency, we must have some common measurement which can be used in the comparison. Fortunately this is available in the determination of absolute loss, or true triglyceride content, of a crude oil which is afforded by either the Wesson or the Chromatographic methods (11). A procedure for the latter is being recommended to the Society for adoption as a tentative method by the subcommittee on the determination of neutral oil in crude oil.

To determine the refining efficiency of any method as applied to any oil, the yield of dry neutral oil in percentage is divided by the neutral triglyceride content of the crude oil (12). Except in the special cases of coconut oil and degummed soybean oil refined with phosphate additives, the open kettle shows the lowest refining efficiencies. On cottonseed oil the two-step refining processes are usually superior in refining efficiency to conventional caustic. For crude soybean oil and linseed oil there is little to choose in refining efficiency between Conventional Caustic operation and two-stage operation. Although the refining efficiency of miscella refining on cottonseed oil is high, we do not have sufficient data to make a valid comparison with other methods of continuous refining. Available data on corn oil would indicate that the two-stage methods are superior to conventional caustic at least in general.

When a study of refining efficiency of the various refining methods now available is made, it becomes obvious that the spread between neutral triglyceride in the crude and neutral triglyceride recovered has now become quite narrow. For example, in the case of crude soybean oil, refining efficiencies upwards of 99% have been obtained by commercial processes, and, on degummed soybean oil, refining efficiences often exceed 99.5%. Therefore, in our opinion, future developments in the refining field will be directed to improving the quality of the refined oil produced and at the same time maintaining the high yields of the best of the refining processes now available. We believe that miscella refining offers great promise in this direction. It is possible to obtain miscella-refined oils so low in bleach color that it may be possible for a shortening manufacturer, purchasing such oils, to eliminate bleaching these refined oils ahead of the converter. This would be a source of considerable monetary saving.

The operating cost of miscella refining should be lower than that of refining at another location than the mill. The same labor force which is employed in the extraction plant handles the refinery, and the by-products in the form of soapstock can be disposed of in the meal.

Another method of refining vegetable oils which, so far, has been held back by its very heavy initial cost but which is technically sound, is decolorization by means of liquid-liquid extraction with propane

(13). Decolorization with liquid propane is a physical, rather than a chemical, process, and it is possible to recover both oil and minor constituents unchanged. The process depends upon varying degrees of solubility of the components of a vegetable oil in liquid propane at temperatures and pressures near the critical point. Unsaponifiable matter and free fatty acids are most soluble, then the triglycerides, and finally the phosphatides and coloring matter. It is therefore possible to pass a crude oil, such as soybean or cottonseed, into an extraction column filled with liquid propane, a flow of which is maintained through the column at a rate of 20 times the volume of oil being treated, and to decolorize the crude oil effectively.

Free fatty acids, unsaponifiable matter, and neutral triglycerides in propane solution are obtained as an overhead fraction, and the coloring matter and phosphatides as a bottoms fraction. The relative proportions of decolorized overheads are 97%–98% of the crude oil fed, and the bottoms, 2%–3%.

The overheads fraction can be produced at colors of 3.5–5.0 red Lovibond, and contains no phosphatides. However the overheads do contain the true fatty acid of the crude oil, and this must be removed before final processing into shortening or salad oil.

Since the decolorized oil is entirely free from break materials it is possible to remove the free fatty acid almost completely by steam stripping without substantial deodorization of the stock.

Although the propane decolorization process has been available for some years and has been applied on the commercial scale to the decolorization of yellow grease and to fish oil, no installation on vegetable oils has been made. However the practicability of the latter has been established by extensive work on the pilot scale. This process still is of great interest to refiners of vegetable oil, and sooner or later it will be applied to decolorization on a commercial scale.

Another process of refining which seems to hold some promise for the future is the use of ion exchange resins for the neutralization and decolorization of crude vegetable oils. The process has been investigated in the laboratory for a number of years, but to date no commercially practicable means of employing it on a plant scale have been devised. Nevertheless we consider the ion exchange process to have promise for the future.

Bleaching

The bleaching of vegetable oils is usually accomplished by treatment with neutral, or activated clays. Chemical treatments, which depend upon the destruction of the pigments by oxidation, have been tried, but none has ever been conspicuously successful. If the oxidizing agent is powerful enough to attack the pigment, it is likely to oxidize at least a portion of the triglyceride, which is highly undesirable in oils which are destined for human consumption.

Some oils, notably red palm oil, can be decolorized to a considerable degree by heat alone, due to the destruction of the carotenoids and other red pigments. Hydrogenation will also reduce the color of oils although in this case if green coloring matter, notably chlorophyll, is present, it will be unaffected. This effect is particularly noticeable in the case of soybean oil, in which red color is readily removed by hardening and by heat bleaching; but after treatment the oil has a pronounced greenish cast when liquid, and if texturated for shortening, its solid color is, at best, a grayish white with a distinct green interior color.

Natural bleaching clays are efficient in removing the red pigment from refined oil while activated clays will remove both types. This property of the activated clays has resulted in their very widespread usage, particularly for the bleaching of refined soybean oils.

The mechanism of earth bleaching has been studied in some detail and is apparently due to the adsorption of the color bodies on the surface of the finely divided clay. Traces of soap and moisture are also removed from the oil in the bleaching process.

The natural clays are, of course, less expensive than those which have been acid-activated and dried, but they are less potent bleaching agents. Generally speaking, their oil retention is less than that of acid clays. A natural clay will retain approximately 0.3 lb. of oil per pound of adsorbent used while an activated earth will retain approximately 0.5 lb. of oil per pound. The natural clays have a tendency to reduce the F.F.A. of the refined oils slightly while the activated clays, on account of their low pH, are likely to increase it.

The activated clays can also be used to bleach certain oils containing substantial amounts of F.F.A., such as red palm oil and completely degummed soybean oil. Several years ago, when large supplies of red palm oil were available for shortening, it was customary to bleach the crude oil with activated earth and then refine the bleached oil. Soapstock from the refining was very light in color and could be used directly in toilet soaps or white soap powders while the soapstock from the crude was too dark for this purpose. Even more important, if the oil were refined before bleaching, the amount of activated earth required to bleach it would raise the F.F.A. beyond permissible limits for edible stocks, and it would have to be given a wash with dilute caustic, thus increasing the loss.

Recently the bleaching of crude water-degummed soybean oils has been carried out on a commercial scale. It is possible, using activated earth, to bleach a completely degummed bean oil to low color and then strip out the residual F.F.A. with steam in a special deodorizer. Or, if the oil is to be hardened for a shortening base stock, it can be hydrogenated before stripping the acid. Thus the step of caustic refining is eliminated. However, in practice, it has been found that the finished oil, either hardened or unhardened, does not have quite the keeping qualities or absence of flavor reversion which is characteristic of oils that are caustic-refined.. Work along these lines is continuing, and it is quite possible that finished products of high quality may be obtained from bean oil by this method.

Domestic natural clays will bleach oil, particularly cottonseed oil, effectively at temperatures under 100°C. Activated clays however work best at temperatures in the neighborhood of 120°C. For this reason the old method of bleaching in open kettles has been largely superseded by vacuum bleaching, which minimizes the effect of oxidation at the elevated temperatures required and also gives lighter colors for the same clay dosage.

It is well known that clay, which has been used once for bleaching an oil, has considerable residual bleaching power, and theoretically this phenomenon would make continuous countercurrent bleaching attractive from the point of view of earth economy. However this does not work in practice, as was demonstrated in the following series of small-scale experiments, carried out some years ago.

A sample of choice refined cottonseed oil, with an A.O.C.S. standard bleach of 1.6 red, was selected. The oil was vacuum-bleached in glass with the amount of earth required to check the standard bleach. The charge was cooled to 60°C. under vacuum and the earth was filtered from the bleached oil. Great care was taken to see that no air was pulled through the filter cake to avoid any oxidation. The cake was immediately slurried with a fresh batch of the same refined oil, and the mixture was heated under vacuum and treated as before. The bleached oil had a color of about 2.5 red.

The percentage of fresh earth which was required to bring the color down to 1.6 was determined and proved to be only 0.1%–0.2% less than the amount of fresh earth required to give standard bleach color in the first place. This experiment was repeated with other refined oils, and the results checked quite closely.

Today the old open kettle method of bleaching has been almost altogether abandoned. Modern, batch, vacuum-bleach kettles are usually designed to take a charge of 30,000–40,000 lbs. of refined oils and are equipped with efficient mechanical agitators and coils that can be used either for heating or cooling. A vacuum of 26.0–27.5 in. is maintained by a two-stage ejector system.

The oil is charged to the bleach kettle at approximately room temperature and the vacuum system started. The requisite amount of earth is sucked into the kettle under vacuum, and the steam is turned into the coils. The temperature of the charge is raised to 110°–120°C., and agitation is continued under full vacuum for about 30 min. The charge is then cooled under vacuum to 50°–60°C., the vacuum broken, and the spent clay filtered out in conventional plate and frame filter presses, of either the open or the closed type.

Several methods of recovering oil from the spent clay have been developed. Blowing with air and steaming will reduce the oil content of the spent cake to 25%–35% on a dry basis, depending upon the earth used. A few plants have installed equipment for the extraction of spent earth with hexane or heptane. In this case any blowing of the press, except to eject free oil trapped between the leaves, is dispensed with in order to minimize oxidation and discoloration of the recovered oil. The trick is to get the spent cake into solvent as quickly as possible, and, if this can be done, it has been found possible to recover oil of a quality almost equal to the bulk of the bleached stock.

Solvent extraction plants for spent cake require a considerable initial capital investment and cannot be justified in many refineries, especially those operating on a five-day week, for, if the spent cake is allowed to stand for any length of time, rapid oxidation will set in and the extracted oil will be very dark in color. Further this dark color is fixed and is very difficult to remove either by re-refining or by re-bleaching.

A light earth bleach is generally used in most shortening plants to remove traces of nickel soaps from hardened base stocks. Usually a few tenths of earth only are required. In some cases, notably with cottonseed oil, where base stocks are hardened separately, it is customary to hydrogenate choice bleachable refined oils without bleaching and pick up the desired color with a relatively heavy post-bleach.

Another adsorbent which finds a use in the bleaching of vegetable oils is activated carbon. It is particularly effective in combination with bleaching clays in the treatment of lauric acid oils, especially coconut oil. Although carbon itself has but little effect as a bleaching agent on cottonseed oil, in combination with earth it is sometimes useful in effecting increased color stability of the bleached oil. In this case the amount used is approximately 10% of the earth dosage.

There has been considerable interest in a continuous bleaching method, and equipment has been designed and installed in a few refineries, where it has been operating satisfactorily over a number of years. King (14) and Singleton and McMichael (15) have described two such methods in detail in papers presented before this Society. Advantages claimed are flexibility in operation, saving in floor space, and economy in earth usage. In cases where the continuous bleaching equipment replaces the obsolete open kettles, both earth economy and improved quality of the bleached oil will justify its installation. The same is true of a new refinery. However where efficient batch vacuum bleaching is already available, it is hard to justify scrapping the existing kettles in favor of the continuous method.

In the future we believe that continued efforts will be made along the lines of chemical bleaching, especially for industrial oils, where a slight amount of oxidation and/or polymerization is not undesirable. It is also likely that improvements in preliminary decolorization of crude oils will lead to the further development of the steam stripping of oils to free them from fatty acids for both industrial and edible purposes. And, of course, there will be continued effort to improve continuous earth bleaching to the point where it can obsolete existing vacuum batch equipment. Or some entirely novel method for decolorizing vegetable oils may be worked out. Certainly it would be a mistake to assume that the limits of human ingenuity in this field have now been attained.

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