Refining of Oils and Fats[1]

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Abstract

The technique of continuous refining of oils and fats has steadily improved since the first commercial installation some 30 years ago. Refining is the most important economic factor in the overall processing of an oil from the crude to the finished product.

Crude oil handling, reagent selection, mixing, heating, and centrifugal separation are all critical when an attempt is made to obtain the maximum refining efficiency. The agronomist, scientist, control laboratory and operating personnel, along with the equipment manufacturers, have all aided in obtaining more efficient and economical processing methods.

In a discussion of the over-all refining process, soapstock handling must also be considered. In recent years several successful continuous soapstock acidulation plants have been installed. With this addition to a refinery, the refining operation can now truly be considered as a continuous process. Like most industrial processes, this has been an evolution from the batch system to a semicontinuous system up to the present continuous treatment of soapstock and wash water to produce a high-purity acid oil on an economical basis.

Details of the various factors in refining and acidulation on a commercial basis, along with control methods, are discussed.

Introduction

Refining of crude oils and fats is one of the most important steps in the processing of these products. Refining frees the triglycerides from undesirable impurities, principally free fatty acid, phosphatides, and other minor constituents. In this step the oil is prepared for further processing into the finished product. Efficient refining removes impurities which are deleterious to the final product and at the same time produces the highest possible yield of refined oil. The refining operation can thus make a dramatic saving in cost.

Refining for years was considered an art and even today may still be considered an art in which science has added a helping hand. There is no ideal criterion for the refining operation as it depends on the finished product desired by the particular company. Continuous refining has been a commercial reality since 1932. One of the first descriptions of a continuous process was presented by James (15) in a paper entitled "A New Continuous Process for the Refining of Vegetable Oil." The basic system was termed "conventional caustic soda refining." In this system a solution of sodium hydroxide was mixed with crude oil in sufficient amounts to remove the undesirable products and at the same time produced a high yield of neutral oil.

Since the original caustic soda method there have been other systems proposed for refining oils to give higher yields. The most widely used of the newer methods is the sodium carbonate process (5), developed around 1940. Essentially this was a two-step process where definite amounts of a soda ash solution were reacted with the oil, and the resulting mixture was dehydrated prior to centrifugal separation. Since soda ash does not effectively reduce the color bodies, the oil was then reacted with a strong caustic soda solution as a re-refining step and then again centrifugally separated. Details on this system have been aptly described by Mattikow (21), Tyler (51), James (17), and others. Later modifications of the soda ash system were developed whereby the troublesome dehydration step could be avoided, such as the modified soda ash process (32) and the pressure soda ash system (38). These modifications came along in the middle 1950's.

Another commercial system developed was the caustic soda-soda ash process, which was also a two-step operation. In this system nearly stoichiometric amounts of caustic soda were added to neutralize the free fatty acid. Prior to separation, sufficient amounts of sodium carbonate solution were added to give the proper consistency to the soapstock to facilitate discharge from the centrifugals. Again this oil was subjected to a caustic soda re-refining stage for color removal (6,23). Essentially in the same period the ammonia process, principally used for the refining of soybean oil, was developed. This process, also described in the literature (23,38), was carried out by reacting ammonium hydroxide with the oil, followed by centrifugal separation. Again a second step of caustic soda re-refining was required for color removal. An interesting feature of this process was the claim that soapstock acidulation was eliminated. By removing the ammonium hydroxide from the soapstock, a highly concentrated phosphatide product was produced.

As mentioned, the first commercial continuous method for refining oils some 34 years ago was the caustic soda process. Although modifications of this method have been used and many other alkalies suggested, it is interesting to note that currently this basic process is still highly favored. A survey of the refiners both in the United States and abroad has shown that the vast majority are currently utilizing the conventional caustic soda process essentially in the same form as that initially described by James (15). This is indeed a tribute to a person's ability.

To analyze the caustic soda refining process and the changes which have occurred since its first installation, extracts of the first paper on this subject are presented. "The process is simple in its essentials and for its mechanical operation depends upon four component parts. These consist in a proportionometer for accurately proportioning two continuously flowing liquids one to the other, a mechanical mixer, a suitable heater for rapidly raising the temperature of the mixture of oil and lye, high-speed centrifugal separators for continuously separating neutral oil and soapstock."

Of interest also is the statement regarding the centrifuge. "The machine is completely enclosed, thus preventing the escape of oil and caustic vapors, minimizing the aeration of the oil."

Actually in this early process the refined oil from the continuous centrifugal stage was usually water-washed in kettles. However this early paper describes a continuous water-washing system as an adjunct in which hot water in amounts of about 10% by weight is thoroughly mixed with the mixture and heated to 165F; continuous centrifugal separation follows. At that time the continuous process was commercial for such soft oils as cotton, corn, and peanut.

Successful pilot plant runs had however, been undertaken on both domestic and imported soybean oil as well as linseed oil. Further, pilot plant runs had been done on continuous refining of hard oils such as coconut, palm, and palm kernel with the remark that research along these lines was being continued. A study of the original patents (14) as well as the early papers will show basically the same system as today's. Now better refining is achieved with far greater efficiency, however. This improvement may be attributed to a) a better understanding of the processing problem through increased scientific technology, b) better performance from such new equipment as proportioning devices, pumps, instrumentation, and centri-

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fuges, and c) a superior crude oil product which has been produced as a result of extensive study by agronomists as well as superior means of harvesting the seed and processing at the mill level.

Basic Principles

Since the majority of refiners are now using the conventional caustic soda process, this paper will concentrate on details in this system for refining vegetable oils principally for edible purposes. The same basic principles will apply for other oils and fats.

Briefly, the crude oil is continuously mixed with a dilute caustic soda solution and, heated to obtain a break in the emulsion; the soapstock is separated from the oil in continuous centrifuges. The refined oil is then mixed with hot water and again centrifugally separated to remove small amounts of soap and other undesirable products. The water-washed refined oil, containing traces of moisture, is then sent to a continuous vacuum-drying stage and on to storage. This procedure is simple, but sometimes important factors may be overlooked. Some of these are itemized: crude oil storage, crude oil feed tanks to process, temperature of both crude oil and reagent, amount of reagent as well as concentration, method of introducing the reagent into the oil, agitation or mixing of reagent with the oil, heating of the mixture to obtain the initial break in the emulsion, distribution and entrance into the high-speed centrifugals, zone control within the centrifugals, and prevention of aeration during processing as well as centrifugation.

The water-washing stage will be considered later. Each phase of the refining process will be separately analyzed and then integrated into the overall process.

Crude Oil Storage and Blending

The crude oil tank farm as well as the blend feed tanks are essentially the beginning of a successful refining operation. The crude oil, as received, in barge, tank car, or truck must be properly sampled and then analyzed by the laboratory. The crude oil may then be segregated by color, refining loss, or even past history of the supply source. It is advantageous to equip each storage tank with an agitator and essential that each blend tank or refinery feed tank be equipped with an agitator. Usually a slow speed side-entering type is sufficient. It is common practice to size the refinery feed tanks at a capacity sufficient for a 24-hr continuous run. By using several feed tanks, representative samples of the oil may first be analyzed in the laboratory to provide information necessary to set up the proper refining conditions.

Because of the current trend for obtaining not only a high refining efficiency but also a high quality product, nitrogen blanketing of the crude oil storage and blend tanks may well be considered.

Selection of Lye for Refining

In caustic soda refining the selection of sodium hydroxide (lye) both in the amount and the solution concentration is extremely important. The amount of lye solution added to the oil is termed the "treat." The correct treat is one which will remove the undesirable impurities in the oil and still give the highest refining efficiency or recovery of usable oil. The sodium hydroxide in the form of a water solution will react with the free fatty acids and, if in excess, with the phosphatidic material as well as with a portion of the triglycerides.

Color bodies are removed either by absorption in the soap formed from the reaction or by absorption directly in the lye solution. Many theories have been advanced as to the reaction of sodium hydroxide with fatty acids, phosphatides, neutral oil, and other constituents. These are important in theoretical considerations. However, to the practical refiner, knowledge of the exact rates of reaction are not important. Again, refining is still an art and not an exact science, principally because of the reactions occurring in a complex organic mixture.

The more common strengths of lye used in refining vary between 8 Be′ and 30 Be′ and more usually in the 12 to 20 Be′ range. The lye solutions are usually prepared from a liquid 50 or 70 Be′ sodium hydroxide solution. The concentration of these solutions as percentage sodium hydroxide for each standard Be′ lye are shown in published (1) tables. The lye solutions may be prepared and held in separate reagent tanks or may be continuously diluted from the concentrated caustic soda solution during the refining operation.

The amount of treat required is based on the free fatty acid of the crude oil plus an excess based on experience. In the United States this excess is normally expressed as an additive amount whereas in Europe it is common to express it as a percentage over and above the theoretical. Bailey gives detailed tables on the lye required to neutralize a specific amount of free fatty acid. There are also tables to determine the excess lye for various Be′ solutions. Although tables are useful, one should always know the means of calculation, for example, a crude cottonseed oil with 1.0% free fatty acid is to be refined with 0.3% excess of 16 Be′ lye.

Form**ula**

$$\%\ \text{Treat} = \frac{(\%\ \text{FFA})\,(\text{factor}) + \%\ \text{excess}}{\%\ \text{NaOH in lye}/100}$$

$$\text{Factor} = \frac{\text{Mol wt NaOH}}{\text{Mol wt oleic acid}} = \frac{40}{282} = 0.142$$

% Excess calculated as dry sodium hydroxide

$$\%\ \text{Treat} = \frac{(1.0 \times 0.142) + 0.3}{11.06/100} = \frac{0.442}{0.1106} = 4.0\%\ \text{by wt of 16 Be}'\ \text{lye}$$

As mentioned, in Europe the excess is usually expressed as percentage of the theoretical which, for the above example by using the same treat, would be calculated as follows:

$$\%\ \text{Treat} = \frac{(\%\ \text{FFA})\,(0.142)\,(\text{excess})}{11.06/100}$$

where, to be mathematically correct,

$$\text{excess} = \frac{100 + \%\ \text{excess}}{100} = (210\%)$$

The actual treat for any individual oil depends on the free fatty acid content, the color desired, the past history of the oil from a particular mill as well as the refining equipment available. A visit to the various refineries throughout the world will show vast differences in equipment and equipment arrangement.

As a guide, usually such soft oils as soybean, peanut, corn, safflower (26), and sesame, which do not present difficult color problems, can be readily processed with 12 Be′ lye. Normally the treat will be from 0.15% excess to 0.30% excess (expressed as additive excess). Cottonseed oil of the usual grade produced in the United States will usually refine satisfactorily with a 16 Be′ lye with an excess varying between 0.3% to 0.6%. Generally this will produce a good yield as well as a suitable color.

The lauric acid oils, coconut and palm kernel, are refined in a different manner from the usual soft oil. Since the principal contaminant in these oils is fatty acid, a more scientific approach may be considered for calculating the treat (42).

A word of caution is given concerning the free fatty acid for these hard oils. It is common practice in the United States to calculate the free fatty acid as % oleic even though the principal acid is the shorter-chain lauric acid. For these oils the efficiency of refining is a factor based on the fatty acid. As an example, it may be assumed that a crude coconut oil has an FFA (as oleic) of 4.5%. This free fatty acid, as lauric, would be 3.2%. It is entirely possible to refine an oil of this type with a plant loss of 4.0%. The seemingly unreasonable refining factor, based on oleic, would be 4.0/4.5 or 0.89. This would appear to be lower than theoretical although actually it is only the method of calculation.

Proportioning

The original proportioning device for refining was a double inter-locked piston pump, positive but pulsating. This served its purpose well and fit in with the other equipment of the time. Although the same basic process is still in use today, more efficient proportioning along with high-speed centrifugal separators have been developed. The present trend is to use ratio controllers to continuously proportion of a smooth reagent flow to the oil.

The amount of reagent is still gauged by rule of thumb. Therefore extreme accuracy is not the criterion of proportioning equipment. The most important consideration is smooth, reproducible flow without pulsations. Many commercial refineries have been studied where the reagent was apparently flowing to the oil in a smooth fashion—at least it seemed so from observing the reagent pen on a circular chart. Actually the reagent flow was pulsating violently because of valve fluctuations, but the instrument was dampened, with the chart indicating a smooth line. Instrument manufacturers are now able to install ratio units with proportional band, reset, and rate action which, with proper valve sizing, will deliver a nonpulsating reagent flow to the crude oil. It is recommended, however, that an indicating rotameter be placed in the reagent line for visual observation as well as emergency control.

A method has been described by Mattikow (22) for determining the reagent flow under plant operating conditions. It is good practice to regularly check the reagent delivery. When refining losses are determined by the sodium balance method (11), the reagent rate would be determined as part of the analyses.

Mixing

After the lye is proportioned into the crude oil, it must be mixed to insure thorough contact with the fatty acids, phosphatides, and color bodies. Mixing in itself has been difficult to reduce to a definite science. This is especially true in vegetable oil refining where thorough mixing is desired without forming tight emulsions. Over the years there have beeen numerous methods proposed for obtaining good contact of the reagent and oil without causing excessive reaction with the triglycerides. On one extreme, there have been the exponents of mild mixing for a relatively long period of time while the mixture is at room temperature. On the other extreme, there are those who advocate short contact-time, violent agitation at elevated temperatures.

And, of course, there are various degrees of mixing within these ranges. One of the first successful continuous refining processes introduced in the United States utilized a horizontal compartmented mixer with paddles in each compartment. Provisions were made also to inject the caustic reagent into any or all of the compartments. With a constant speed drive it was possible to vary the time of contact between the reagent and the oil. This basic compartmented mixer was later modified by introducing a variable-speed drive, changing the shape of the paddles as well as adding bafflles in the compartments.

Another widely used mixer, introduced at a later date, was a vertical tank type, which usually employed disc and donut baffles with the agitator blades between the baffles. One of the earlier continuous refining installations used a series of these vertical mixers with a steam jacket on each mixer. In this system the reagent was added to the oil prior to entering the lower section of the mixer. By employing several mixers in series, various degrees of contact could be obtained as well as specified temperature ranges during contact of the reagent with the oil. Again this mixer was modified by adding a variable-speed drive and modifying the baffles as well as the paddles.

Undoubtedly more experimental work has been performed on the mixing of crude cottonseed oil and reagent than on other oils. This was primarily due to the color removal problem on dark cottonseed oil. Numerous theories have been advanced as to the most satisfactory method for removing maximum color and obtaining high refining efficiency. As pointed out by James (17), there are those who contend that color removal is effected by absorption of the color bodies in the soap in the refining mixture and that it is even necessary to produce additional soap by some saponification of the neutral oil so that absorption may take place. There is also the theory that color bodies in a crude oil are soluble in the caustic solution, and therefore excess caustic is required for this absorption.

With particular reference to cottonseed oil, it has been my experience that color bodies may satisfactorily be removed by long contact at room temperature by using relatively mild agitation. Under these conditions a low excess of caustic is utilized to prevent excessive saponification of neutral oil.

Undoubtedly there is the possibility of improving the mixing phase of the refining operation. As indicated in the literature, several commercial installations used a method which consisted of using supersonic vibrations over a short period of time to put the caustic in contact with the oil. Although this method appeared to offer some interesting possibilities, it apparently was not readily accepted by the industry. Other data have been studied, principally from a laboratory viewpoint, which indicates that oil particles, when in contact with caustic, may become coated with a layer of soap which acts as a barrier to further reaction with the reagent. When this phenomenon occurred, the reagent could no longer react or absorb the impurities within the oil particle itself. The preliminary data indicated that there was an optimum size for the particle as well as an optimum time for contact. Undoubtedly a team approach, for example, a chemist, an engineer, and a microscopist, could lead to some interesting and valuable answers on this phase.

On oils which do not present a color problem, for example, soybean and peanut, mixing may be held to a minimum. This is particularly true when the refined oil is to be followed by hydrogenation and deodorization or only deodorization.

With the lauric acid oils, such as coconut and palm kernel, mixing becomes extremely critical because of the problem of excess emulsification which results in difficult centrifugal separation (42).

The present-day commercial refinery which handles both soft oils and hard oils must have versatility in mixing in order to be successful. The usual equipment consists of three or four either horizontal compartmented mixers or vertical disc and donut mixers connected in series with a provision for bypassing one or more, depending on the oil being processed. For the sensitive lauric acid oils, usually all of the conventional mixers are bypassed and a short contact mixer is employed. This flexibility is easily accomplished by utilizing suitable piping connections when the proper equipment is available.

An interesting and often overlooked phenomenon may occur during the mixing of caustic with the oil. In the discussion of proportioning a nonpulsing reagent flow to the oil was emphasized. In actual refinery practice a pulsating caustic delivery has been observed to carry through an entire bank of mixing equipment and to result in poor centrifugal separation because of varying densities in the oil mixture itself.

Heating

There are two stages in the primary refining of an oil where heating is important, namely, preheating and postheating. Preheating, as the name implies, is heating the crude oil prior to the addition of the caustic treatment. While preheating may not be utilized as much as postheating, it is just as critical and important.

A common method, when preheating is utilized, is to heat the oil in the refinery feed tank. This practice, however, is not recommended as it is difficult to maintain a constant temperature and there is the problem of oxidation, which is caused by the exposure of a large surface of oil to the atmosphere under elevated temperature conditions. When preheating is required, the preferred method is to maintain the oil in the refinery feed tank at ambient temperature and to utilize a heat exchanger, with accurate temperature controller, for elevating the oil to the desired reaction temperature prior to caustic addition. Sufficient velocity must be maintained within the heat exchanger to prevent deposition and subsequent burning of the product.

Postheating is the heating of the oil-caustic mixture after the mixing stage. The purpose of heating after mixing is to create a thermal shock to the mixture which assists in breaking the emulsion of the oil-caustic-soap mass. The common term used in refinery practice is to form a "break" in the oil mixture. The proper break in the emulsion is of utmost importance for the highest efficiency in centrifugal separation.

It is usual practice to insert a sample cock in the piping system prior to the centrifugation stage. Means for obtaining a visual observation of the break are desirable when an unfamiliar crude oil is refined.

The design of heat exchangers as well as instrumentation can be critical to the centrifugation stage. The purpose of heating after mixing is to obtain a break in the emulsion. Without proper design in the heating stage, this purpose may be defeated. A close control on temperature is also important as a fluctuating temperature would cause a fluctuating density. Changes in density caused by temperature as well as those caused by improper caustic addition will result in density changes within the centrifuge.

It is well known in the industry that copper-bearing alloys must not be in contact with the oil (33). However, in the heating stage, occasionally this has been overlooked with such seemingly simple items as thermal bulbs for temperature regulators and sample cocks (9). A factor also to be considered is the sizing of the heat exchangers to insure proper velocity through the coils to prevent deposition on the heat-exchanger walls and at the same time to assure nonturbulent flow to aid in conditioning prior to centrifuging. If the commercial refinery is to be operated at reduced capacities for any period of time, it is preferable to design the heat exchangers in parallel banks whereby portions may be bypassed when necessary.

It is considered good refinery practice to provide means for periodic cleaning of the heat-exchanger surface. A clean-in-place operation (CIP) may be utilized by providing the necessary piping connections for flushing the heat-exchanger surface with a suitable cleaning compound. This will insure uniform conditions and will result in maximum efficiency.

Separation

The separation stage of the refining process is the most important as the results of proper pretreatment and centrifugation now become apparent. It is in the separation step that the yield of refined oil is determined. In continuous refining, high-speed centrifugals are used to separate the oil-reagent mixture into refined oil and soapstock. All of the previous processing has been in preparation for the separation stage.

The centrifugal manufacturers, like other equipment manufacturers, have been improving their design to give both higher capacity per unit as well as more efficiency in separation. The efficiency of separation means the highest possible yield of refined oil or, stated another way, the smallest loss of refined oil into the heavy phase or soapstock phase. Assuming that pretreatment has been conducted properly, the highest separation yield will be obtained only from an understanding of a particular centrifuge.

Centrifugal theory and its application to practical operation have been described in numerious articles (37,39,43). The centrifuge works on a difference in densities between two immiscible materials. In the case of refining, the light phase will be refined oil containing traces of moisture and soap, and the heavy phase will be principally soap, phosphatides, free reagent, meal, and small amounts of entrained neutral oil. Generally it may be considered that each particular type of centrifuge will have a certain neutral zone, which will afford the most efficient separation, depending on the configuration of the centrifuge bowl. To maintain the neutral zone at this particular diameter within the centrifuge requires external adjustments in the outlet parts of the bowl for any change of densities in the feed stocks. Under any one set of conditions, with constant densities on both the light phase and heavy phase, the separation zone may be varied on an open type of centrifuge by changing the heavy-phase diameter and using various discharge rings. On a pressure type of centrifuge (39) the discharge diameters on the outlet parts are maintained constant, but back pressure may be applied to the light phase (or heavy phase) to move the separation zone.

Even under optimum conditions there can never be 100% separation of the products. The aim is to separate the heavy phase with the least amount of entrained oil. To accomplished this it is necessary to allow a small amount of soapstock phase to pass along with the refined oil for subsequent removal in the water-washing stage. When one is visualizing the internals of a high-speed, rotating centrifuge bowl, it becomes apparent that, when the zone is moved toward the outer periphery of the bowl, the light phase will have maximum clarifying time while the heavy phase will have the least clarifying time. As the separation zone is moved toward the center, the opposite effect occurs. It is possible to maintain the zone at the theoretical design diameter under practical operating conditions by means of visual observation of the refined oil as it discharges from the centrifuge.

The refined oil should carry a small amount of impurities, which may be observed by using a lighted sight glass in the oil outlet and visually observing the turbidity or by using one of the modern turbidity instruments. Another method is to use a high-speed, test-tube centrifuge as a control (25). A sample of the oil may be obtained at the discharge of the centrifuge and tested for percentage of solids by volume. The allowable amounts which pass along with the refined oil to the water-wash stage can vary with the individual refineries. Data obtained by using a test-tube centrifuge especially designed for correlation to the high-speed continuous centrifuges indicated that optimum separation could be obtained when the solids by volume in the refined oil were maintained at $0.1 \pm 0.05\%$. This also indicates a satisfactory condition for water washing.

The conclusion may be drawn from these tests that, when the refined oil is brilliant, without solids, there is the possibility that free oil is occluded in the soapstock passing out of the heavy phase and that there will be an excessive loss of product.

If, when the refined oil is too dirty as it discharges from the light phase, it obviously contains an excessive amount of soapstock, which will result in an extremely difficult water-washing operation. This factor will be considered farther along with the discussion of the water-washing stage.

No discussion of the centrifugal separation would be complete without mention of sealing the bowl. In order to operate the centrifuge there must first be a heavy-phase, liquid seal within the revolving bowl. The term "seal," often called bowl prime, refers to the liquid barrier between the heavy phase and light phase outlets. In placing the centrifuge in operation, this seal is first obtained by either adding water or reagent continuously until a discharge occurs from the heavy-phase outlet. The centrifuge bowl now has a liquid seal. At this point the oil-reagent mixture may then be allowed to run through the centrifuge for separation. Normal practice suggests a reduced rate initially and gradually increasing to full flow to avoid a shock within the centrifuge which could result in loss of seal. If seal loss occurs, it means that the entire mixture is then flowing out of the heavy-phase or soapstock side with a resulting high loss of product.

Under normal operating conditions, if the separating zone within the centrifuge is maintained at the design interface, loss of seal will never occur unless some condition is changed in the system. Normal changes in flow rates of either the oil or reagent or the total flow will not materially affect the separating zone. However, changes in the density of the reagent or, as an extreme example, inadvertent loss of reagent flow could cause an upset in the zone.

If loss of seal should occur, the feed to the centrifuge must immediately be stopped and the bowl again sealed

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with either water or reagent. To avoid high loss of product the centrifuge should be equipped with warning devices and preferably automatic shut-off or automatic sealing devices.

In the description of the first continuous refining unit (15), centrifugals were rated at an optimum capacity of 1,000–1,250 lb per hour or approximately one-half tank car per day for the refining stage. With the trend in refining going to higher and higher capacity, many of the modern centrifugals are rated in multiple tank cars per day.

Norris (24) illustrated several commercial high-capacity, continuous centrifugals on the market. The performance of each of these particular models has been described in various technical articles. Recently introduced on the American market and in commercial operation for vegetable oil processing both in the United States and abroad is a high-capacity disc centrifuge. The interesting features of this unit are the two centripetal pumps or paring discs (44) for handling the discharge of both the oil and soapstock from the bowl. The separation zone may be varied during operation by changing the back pressure on the discharge from either of the centripetal pumps. It is claimed that the liquid seal formed by the immersion at the periphery of the pump disc in the product discharges gives a completely air-free action that eliminates the need for mechanical seals (34,49). This modern high-capacity unit is rated by the manufacturer at 25,000 lb per hour (10 tank cars per day) for refining (49).

Fig. 1 shows a cross-section of this centrifuge and illustrates the two centripetal pumps used for discharge of the products. It should also be noted that this unit has means for continuously adding a separate stream of water to the outer periphery of the bowl. It is necessary to add water as a diluent to the lye/soapstock mixture when one is re-refining oil with strong caustic or refining degummed oils with strong caustic. The water, by reducing the density of the free lye in the soapstock, will allow a clean separation of soap from the oil and prevent a three-phase formation within the high-speed revolving bowl.

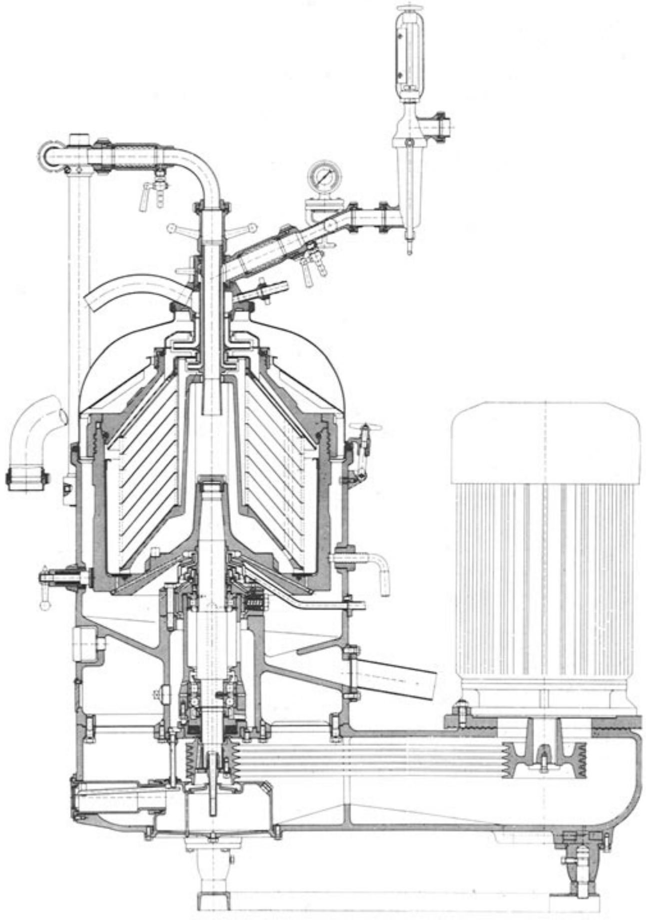

Fig. 1. Westfalia vegetable oil refining centrifuge (courtesy of Centrico Inc.).

Water Washing and Vacuum Drying

The refined oil is pumped continuously from the primary stage of refining to the secondary stage of refining, namely, water washing. The oil is heated to 165–180F and mixed with hot water for washing. The hot water at 190–200F is continuously proportioned to the oil in amount from 10% to 20% by weight of the oil. The oil-water mixture generally passes through a mixer to insure adequate contacting of the water with the soap and other minor impurities. The mixers used at this stage will vary with the individual refiner's choice. Conventional vertical disc and donut baffle units similar to refining mixers have been used successfully. Also, simple mixing pipeline tees have been employed. Several installations have been observed where cut impeller centrifugal pumps were used for mixing.

It is recommended at this stage that adequate mixing be utilized. A combination of a high-speed pipeline mixer, followed by a vertical or horizontal mixer (refining stage type), will insure good contact of the water with oil. There will be no emulsion problems because of this intensive mixing if the refining separation has been performed properly.

The oil-water mixture is passed to centrifugals for separation. The centrifuge discharges the water-washed oil as the light phase, and the water-soap solution along with insolubles as the heavy phase. As discussed under refining, the centrifuge must be operated at the most efficient zone of separation with consideration for zone control, sealing of the bowl, and breakover alarms if loss of seal occurs.

The washing operation may be carried out either as a single water-wash or as a double water-wash. In single water-washing, for example, 15% hot water by weight of the oil may be mixed and centrifuged, as described; the washed oil from the centrifuging stage passes on to vacuum drying. In a properly designed system with adequate control in both the refining and water-washing stage, it is common to remove 90% of the soap, as sodium oleate, in a single water-wash. It has been claimed by one manufacturer of refining equipment that 97% of the soap will be removed in one water wash if 20% water by weight is used for the washing (29).

Many refinery operators prefer a two-stage water-wash system. In this the washed oil discharged from the first water-wash, centrifugal stage is again put in contact with water in the same manner and again centrifugally separated. The usual practice in two-stage water-washing is to employ 10% hot water by weight in each washing stage. Undoubtedly two stages of water washing are more efficient than one stage. It is, therefore, a matter of the economic justification and the purity which is desired.

Mention should be made regarding the water used for washing the oil. Braae and co-workers (3) determined that hard water could be detrimental to the oil stability. Whereas sodium salts are readily soluble in the water phase, salts of calcium and magnesium are essentially oil-soluble. Baldwin and Cowan (33) further emphasize that the water should be free from Cu and Fe. It is claimed that washed, refined oil should contain not more than 0.1 ppm Fe and 0.01 ppm Cu (7,9,12,33). Again as in the case of Ca and Mg, these metals will cause poor stability of the finished product. It may be concluded that water must be treated to prevent contamination of the oil. (Incidentally this also applies to the water used for reagent dilution.)

Fig. 2 illustrates a modern high-capacity centrifuge recently introduced for water-wash separation. The novel feature of this centrifuge is the one centripetal pump (paring device) for the light phase with a discharge ring for the heavy phase. On this unit, the neutral zone is varied by changing the discharge ring at the heavy-phase

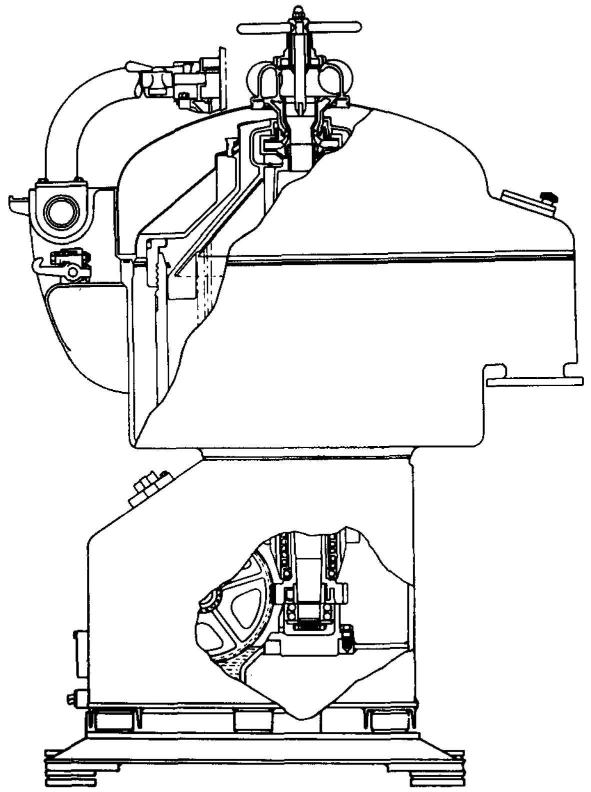

FIG. 2. Cross-sectional view of De Laval water-wash centrifuge (courtesy of The De Laval Separator Company).

outlet when the centrifuge is not running. Since the density of both phases is essentially constant in the water-oil separation (a liquid-liquid separation), changing to different rings is not usually necessary. The centripetal pump on the oil phase acts as the pump in sending the oil to the vacuum dryer. The manufacturer claims that this centrifuge successfully separates at rates of 45,000 lb per hour (18 tank cars per day) in a commercial installation. It is also claimed that the oil losses in this stage, at this high capacity, are only 0.005%–0.02% when the primary refining stage is under recommended operating procedures (27,29).

The water-washed oil after the centrifugal separation, either one or two stages depending on the system, is passed to a continuous vacuum dryer for moisture removal. The most common type in commercial practice is the vertical vacuum chamber with spray nozzles mounted in the upper section for discharging the oil into the evacuated unit. The vacuum equipment usually consists of a two-stage, steam ejector system with intercondenser and occasionally after-condenser producing a 27–28 in. Hg vacuum. The instrument controls on the vacuum drying system will normally consist of high level alarm and shutdown with solenoid valves or air-operated valves on the oil inlets to prevent air coming in contact with the hot oil. Other controls may be added to insure further protection at this stage.

The oil discharged from the vacuum dryer normally contains less than 0.1% moisture, more often in the range of 0.05%, and, if water washing has been carried out satisfactorily, not more than 50 ppm soap as sodium oleate (13). If the oil is to be stored in unprotected tanks, that is, without nitrogen protection, for any length of time, it is recommended that the oil be cooled as discharged from the dryer.

TABLE I

Refining Crude Cottonseed from Different Sources

Source	Cup loss %	Centrifuge loss %	Chromato. loss %	Savings over cup %	True refining efficiency %	Guarantee loss
1	7.4	6.3	3.2	14.9	96.8	4.6
2	7.3	4.5	3.0	26.0	98.5	4.4
3	7.2	6.8	3.1	6.0	96.2	4.5
4	7.1	4.0	3.4	43.6	99.4	4.9
5	6.8	3.6	2.8	47.0	99.2	4.2
6	5.8	2.9	2.6	50.0	99.7	3.9

Evaluation of Refining

There have been numerous methods suggested for evaluating the efficiency of a commercial refining operation. The method most used in the United States has been the comparison of plant loss to the official cup loss. Usually the plant loss is expressed as savings (or gain) over the cup. The cup loss was originally intended as a means of assisting the plant batch-kettle refiner in selecting the most satisfactory treat. Even now that kettle refining is nearly nonexistent, the refining operation is still often evaluated to the cup loss (16).

More recently, plant refining is compared with the absolute theoretical loss as determined by the official chromatographic loss. The efficiency of an operation may be compared with the theoretical where refining efficiency is the ratio of plant yield to theoretical yield.

Since crude soybean oil is now traded on the basis of chromatographic loss and the crudes are also becoming more uniform, refining efficiency will be more widely used. A hypothetical example of refining nondegummed crude soybean oil, by using crude oil analyses from more than 500 tank cars, is used to illustrate the methods of evaluating efficiency. These crude oils gave an average analysis of 2.32% chromatographic loss and 3.75% official cup loss. If this oil was refined in a typical commercial plant with a plant loss of 3.1%, including water wash, the refining efficiency would be calculated as: $R.E. = (100 - 3.10)/(100 - 2.32) = 0.992$ or 99.2%.

This may be considered very efficient refining. If compared with the official cup loss, however, it would appear to be poor refining as the savings over cup would be only 17.3%. This is calculated as follows: $(3.75 - 3.10)/(3.75 = 17.3\%/100$.

To further illustrate loosely applied terminology, a refiner may casually state, "we can do 30% better than the cup." It is soon obvious that he is not specifically referring to a crude oil with the before-mentioned analysis. For a 30% savings over the cup, the plant loss would be only 2.62% or an unusually high refining efficiency of 99.7%, ideal but hardly practical.

Occasionally when one studies European refinery results, the term "refining factor" is encountered. Normally the refining factor is the ratio of actual plant loss to theoretical loss. The theoretical may be expressed as Wesson loss or the chromatographic loss.

Crude cottonseed oils, primarily because of color problems, offer more difficulties when the efficiency of plant refining is evaluated.

Pohle et al. (25) developed a laboratory, centrifugal refining method which was sufficiently analogous to actual plant processing conditions to provide a means of evaluating plant efficiency. Their data clearly illustrated the differences in refining yields when similar crude oils from various sources were compared.

A portion of the data is reproduced in Table I, showing refining loss by different methods for crude cottonseed oils from different sources. Also shown are calculated true refining efficiencies (ratio of actual yield to chromatographic neutral oil), centrifuge loss savings over cup loss, and one equipment manufacturer's typical performance guarantee of loss for oils of this general type (31).

As may be observed from the data, certain of these crude oils, namely, samples from Sources 1 and 3, would appear to be refined inefficiently when rated by either savings over the cup loss or true refining efficiency. Samples of oil from sources 2, 4, 5, and 6, when they are evaluated by either the cup loss or refining efficiency, would be rated as good to excellent.

Actually all of the refinings were performed by the plant in as efficient a manner as possible. For good refining operation, the laboratory and production must operate as a team. This cooperative effort and under-

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• *Refining of Oils and Fats . . .*

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standing between the two groups will result in the most profitable operation for the company. The laboratory, centrifugal refining method developed by Pohle et al., when it is correlated to actual plant processing conditions, provides an ideal means of evaluating plant efficiency as well as of determining the most profitable sources of crude oil. These data also illustrate the difficulty involved with requesting a performance guarantee. A realistic guarantee is only valid for a specific batch of oil which has been laboratory-evaluated.

Data from one commercial plant, refining crude cottonseed oil from essentially one source, is shown in Table II (30). This crude oil mill installed its first continuous refining process circa 1948. The installation was initially a two-stage Clayton soda ash process with single water-wash. In 1957 this plant was converted to the pressure soda ash system (38), still as a 4-tank-car per-day operation. Within the last few years the pressure soda ash process was abandoned, and the plant was converted to the conventional caustic soda process. Since the time of converting to caustic, this plant has steadily increased its refining rate from the initial 4 cars per day up to the present rate of 12 tank cars per day, still utilizing its existing equipment.

The data illustrated is for the period October 1965 through May 1966. The crude oil is extracted from cottonseed obtained in the San Joaquin Valley from the Los Banos area on the north to the Bakersfield area on the south. The seed is known as Acala 4–42 and was developed by the USDA Cotton Experimental Station, Shafter, Calif.

Oil Stability

Stability of the finished vegetable oil product is extremely important. Continual investigation is being carried on, to seek methods for improving the keeping qualties of the various oils. Contact with air as well as certain metallic substances produce poor keeping-quality of the finished product. It is common practice today to protect an oil during the deodorization stage as well as during storage of the finished product after deodorization. Normal practice calls for a metal scavenger, such as phosphoric acid or citric acid, to be added to the oil during the deodorization cycle. It is also common practice to hold the finished oil in stainless steel storage tanks (52) under a nitrogen blanket (47,48).

There is currently a definite trend to handle oils in a similar manner during the initial stages of processing, that is, prior to deodorization. Baldwin (33) has expressed this very aptly by the phrase, "Protect the oil from crude to the bottle."

Braae et al (4,45) presented experimental data definitely showing that the presence of air during the alkali refining and washing had a deleterious effect on the stability of the final oil and that even a relatively small increase in the peroxide content of the refined oil clearly diminished the stability of the deodorized oil. The most stable deodorized product resulted from an oil which was nitrogen-protected during refining. Braae (2) in other work found various additives, especially small amounts of phosphoric acid, effective in producing a more stable final product.

Essentially the same results were reported independently by both Cowan (7,8) and Baldwin (33), based on studies of soybean oil processing. It was recommended that the oil be protected from air after extraction, during storage, before refining, during refining, and afterwards. This same caution must apply as well to elimination of prooxidant metals and to protection from metal contamination by use of metal scavengers during the entire processing. It is again emphasized that 0.01 ppm of copper and 0.03 ppm iron contamination in the oil are sufficient to lower the stability (9).

Currently at least one large refiner in the Southwest is using inert gas (48) to blow all oil lines and presses and is using pure nitrogen for blanketing on finished oil storage and shipment. Another company in the Midwest is presently producing a high-quality refined, deodorized soybean salad oil by the proper use of a metal inactivating agent as well as by nitrogen protection of the product after deodorization (28). This commercially produced oil might best be called "a protected soybean salad and cooking oil" (8,9). It is unquestionably only a matter of time before most oils will be blanketed under nitrogen at the crude mill; the ensuing storage, processing, and final product handling will also be under a nitrogen blanket, from crude to bottle as the ultimate.

Acidulation

The refining process is not complete without consideration of the by-products, namely, soapstock and wash water (36). Originally these products were discarded or, depending on the market demand, batch-acidulated (20). Batch acidulation is one of the most expensive as well as cumbersome processes in oil handling. Over the past 10 years methods have been developed to make acidulation of the soapstock a continuous process (18,19,46). In many respects the development has paralleled the methods in obtaining crude tall oil (40,41).

Todd et al. (50) describe a commercial system whereby soapstock usually diluted with the wash water is continuously processed to yield a good quality of acid oil and a dilute acid wash water. The diluted soapstock is heated and mixed with a continuous proportioned stream of concentrated sulfuric acid. This mixture is centrifugally separated with simultaneous water-washing.

The waste water from a typical soybean oil soapstock, when it is acidulated in this process, amounted to approximately 17,500 pounds per 60,000 pounds of crude oil when refined at a 3.25% loss. The acid wash water from this typical test contained a total of 44,000 ppm dissolved and suspended solids, a BOD of 9,400 ppm, and a mineral acid content of 1.0%.

Crauer (10) describes a continuous process which is claimed to handle all types of caustic soapstock by utilizing essentially the same general process, that is, continuous

TABLE II

Plant Refinery Data for Conventional Caustic Refining of Crude Cottonseed Oil (30)

	1965			1966				
Months	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
Crude oil lb.[a]	1.654	4.089	4.018	4.739	4.502	4.927	4.667	6.372
Refined oil lb.[a]	1.621	3.967	3.898	4.578	4.345	4.755	4.530	6.169
Plant loss %	2.00	2.97	2.98	3.39	3.49	3.47	2.94	3.18
Plant bleach (red)	0.9	0.9	1.1	1.4	1.4	1.7	1.7	1.8
Soap in dry oil[b]	6	8	8	10	10	14	10	10
FFA %	0.4	0.5	0.6	0.8	0.9	1.1	0.7	0.7
Cup loss %	4.16	4.21	4.52	5.35	5.35	5.68	3.93	4.22
Cup ref. color (red)	3.4	3.2	3.4	3.5	3.7	3.9	3.8	3.8
Cup bleach color (red)	0.7	0.6	0.7	0.7	1.0	1.0	1.2	1.3
Chromo. loss %	1.80	1.87	1.86	2.22	2.40	2.43	1.89	1.99
Refining eff. %	99.8	99.0	98.9	98.8	98.9	98.9	98.9	98.8
Savings over cup %	51.9	29.5	34.1	36.6	34.8	38.9	25.2	24.6
Lye as 50 Be' lb.[c]	5,900	17,560	14,500	15,650		56,932		22,220
% Excess over FFA	0.13	0.14	0.10	0.05	....	0.08 Aver.	....	0.07

[a] In millions.

[b] Soap as ppm NaOH.

[c] Total 50 Be' lye used; diluted to 14, 16, or 20 as required.

reaction of sulfuric acid with the diluted soapstock. A novel feature claimed in this process is the control of sulfuric acid by pH cells in the reaction mixture. Another feature claimed is a heat exchanger after the reaction mixer to cool to the acidulated mixture of cottonseed oil soapstock prior to centrifugation. The waste water in this example contained 0.3–0.5% mineral acid and a BOD in the range of 2,400–14,000 ppm. Stahle (35) presented engineering and economic data on the same process, as described by Crauer. It is claimed that sulfuric acid consumption is less than half of that used in the batch system. Consequently the caustic required for neutralizing the waste water prior to disposal will be considerably less than that required in the batch system.

The manufacturer of the process, as described by Crauer and Stahle, claims (29) that recent information from several commercial installations gives even more satisfactory results than previously published. For example, the acid oil from the continuous acidulation of a nondegummed soybean oil soapstock, in a one-stage centrifugal separation, analyzed TFA = 90.0–92.2%, OFA = 1.5–2.0%, moisture = 2.4–5.5%, mineral acid = 0.02–0.05%. The acid waste water, as discharged from the centrifuge, analyzed pH = 2.8–3.0, TFA = 0.013–0.36% with the overall TFA recovery in the acid oil phase of 96.8 to 99%.

When a dry product is desired, the acid oil, as discharged from a continuous centrifuge or settling tower, may be heated to 190F and flash-dried in a continuous vacuum dryer. The resultant product will have a moisture in the 1.0% range.

With the present demands and high market price for acid oil, it is imperative to acidulate the soapstock in the most economical manner to obtain the highest yield. Recent market prices of acid oil were quoted on a 100-pound, FOB basis as $7.50 for cottonseed, $8 for soybean, and $12 for coconut acid oil.

With the advent of continuous acidulation, the over-all refining operation may now be really considered a continuous process. When the operation is planned properly, it will result in an efficient operation that yields high quality products and by-products with a maximum return on the investment.

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ASA Expands Activities to Taiwan, Korea and West Germany

The AMERICAN SOYBEAN ASSOCIATION is expanding its market development activities to Taiwan, Korea and West Germany.

ASA has directed the promotion efforts in Japan for 11 years. Next month ASA's Country Director, Scott Sawyers, based in Tokyo, will conduct a preliminary market survey in bustling Taiwan, in answer to a formal request from the Taiwanese Vegetable Oil Manufacturers Association. Sawyers met with industry leaders in Korea to investigate the possibility of participating in a trade fair in Seoul this fall.

In West Germany a pilot program of promoting identified soybean oil will be tried for the first time in cooperation with the Soybean Council of America. Soybean oil is not identified but sold as a blend around the world. The identified soybean oil will be sold through thousands of retail outlets of the EDEKA food chain, the largest in Germany.

The rapidly expanding Taiwanese pig and poultry industry is creating an increased market for soybean meal. United States soybean sales passed the 10 million bushel per year mark—all in dollar sales. In addition to meal for feed, opportunity exists to increase human per capita consumption of vegetable oil in Taiwan.

In contrast to the Orient, Western Europe has a high edible oil consumption—higher than the U.S.—that is not expected to increase. Soyoil promotion in West Germany aims for a larger share of the present market. Competition is toe-to-toe against other identified vegetable oils such as sunflowerseed oil from Russia.

ASA's entry into Taiwan and Germany is made possible by funds contributed by market promotion agencies in Iowa, Louisiana, Mississippi, Missouri and Ohio. A recent amendment to the contract with Foreign Agricultural Service, USDA, provides funds for program activities in Taiwan and extends financing of the Japanese project through June 1971.

The soyoil promotion is a cooperative effort of the Soybean Council of America and ASA. Joint financing comes from FAS, EDEKA and ASA with administration by the Council.

Council president Glenn Pogeler notes that West Germany is currently the number 2 buyer of U.S. soybeans after Japan. A successful soyoil promotion could significantly increase U.S. soybean sales.