solids discharge ports located at one end of the unit. The solids consist of approximately 61% water, 26% protein, and 13% fat. The liquid fat, with some unrendered material, is then run through a comminutor to complete the rupture of the fat cells and insure satisfactory operation of the centrifuge valves on the subsequent clarification. The comminuted fat is heated to 195–200°F. and pumped to an autojector clarifier centrifuge. This is a centrifuge which is equipped with a series of automatically operated valves located around the periphery of the bowl to discharge solids automatically. The accumulation of solids in the bowl causes the valves to open. When the solids have discharged through the open ports, the valves close. The water and protein are removed from the fat, and the fat is discharged to storage. The solids accumulated from both centrifuges may be collected and dry-rendered for final recovery of fat and protein.

There are a few other methods of rendering, such as open kettle and various modifications, but they are not important, and to cover them would be largely looking backward.

There are still numerous problems to be solved in both wet and dry rendering, but the last few years have been encouraging in that definite attempts have been made to solve some of them with a moderate degree of success. It is hoped that with a wider understanding of the rendering processes, more progress will be made.

Vegetable Oil Refining

FRED H. SMITH, The Sharples Corporation, Philadelphia, Pennsylvania

I WOULD LIKE TO QUOTE from a paper presented before the North Central Section of the American Oil Chemists' Society in Chicago about 18 months ago. "Within the memory of most of this audience tonight, refining of vegetable oils was accomplished by kettle refining or a single version of caustic centrifugal refining. Each in its own way was an art, and profits depended on that art centered in an experienced refiner who tasted oils, rubbed soapstock in his hands, and blamed the crude mills for a poor extraction."


F. H. Smith

It was pointed out that today no processor can afford this luxury. To survive he must critically analyze some seven different refining methods in terms of his own unique requirements and operate a plant best suited to solve his problems of particular crude oils available, oil quality specifications, water supply, sewage disposal, and utilization of gums and soapstock.

Now however this list of possible process selections has grown to nine. How many more will be introduced depends on how many experimenters can and will spend the time and money required fully to develop new systems and to present an account of the completed research to the industry. The problem has become quite complex and may be expected to become more so.

The purpose of this paper will be to assist in completely understanding each new process as it develops and to analyze some of the existing systems in terms of the information available. This discussion will not deal with specific equipment selection but will bear on the following points: classification of contaminating components—how refining losses and oil quality are affected by removal of these components; classification of seven process concepts in terms of refining losses and quality; the physical chemistry of refining as applied to the process concepts; and examples of refining results selected from United States and Mexico.

Contaminating Components

The contaminating components in a crude oil are phosphatides or gums, free fatty acids, color, moisture, and meal and dirt.

Gums represent the natural phosphatidic materials contained in the crude oils. Some oils, such as palm or coconut, have so little of this contaminant that conditioning or removal need not be seriously considered. On the other hand, the American oils, such as cottonseed and soya, contain from 1 to 2% gums which must be removed to produce a refined edible or technical oil.

To a large extent, the gums are soluble in dry crude oils but may be precipitated as a non-oil soluble sludge by hydrating with water. The precipitate is a gelatinous mass wherein oil is dissolved in the gums. They are easily separated from the oil by centrifugal or gravity means, but in so doing the dissolved oil of the gums cannot be reduced. The percentage of oil in the gum phase seems to be a strong function of the water treat used, which is important for other reasons to the producer of technical oils. In general, a low water treat of 1% or less will produce gums which dissolve no more than 15 to 25% oil, giving gums of 75 to 85% acetone-insoluble rating. Higher water treats will increase the ability of the gums to dissolve oil but at the same time will do a better job of removing the last traces of gums from the oil. For the technical oil producer the right compromise between loss and gum removal becomes the basis for his profits.

However for the producer of fully refined technical oils or edible oils, percentage of treat is usually selected for other reasons. Gums must be fully removed to protect taste and flavor, but they need not be removed separately.

The following generalities emerge as important to developing a refining process. Gums dissolve oil, thereby reducing the importance of high separating forces or long separating times as means of reducing degumming plant losses. Chemical additives must be used to change the nature of the gums before losses lower than those inherent in water degumming alone can be achieved. To mention a few, citric acid, phosphoric acid, acetic anhydride, tetra sodium pyro phosphate, and sodium silicate have all been used to some extent.

Fatty acids exist to some extent in all natural crude oils. By some means they must be removed, whether it be by distillation or neutralization into a soap, followed by mechanical separation. Since distillation is not generally practiced and is rather specialized in its application, this paper will deal only with neutralization into soap.

Many bases and salts of strong bases have been used, caustic, soda ash, ammonia, and trisodium phosphate to name a few. The problem, of course, is to select a neutralizing chemical which will have no side reactions deleterious to refining, such as destroying valuable triglycerides through saponification, or so to adjust the use of the chemical selected that possible side reactions are minimized or eliminated.

Equally important however is the fact that the soap produced is a spongy mass which can entrain neutral oil rather than absorb it in solution. In this respect centrifugal refining has demonstrated its value in squeezing the oil from soapstock, and the highest possible force available for this purpose pays dividends in more refined oil and less oil in the soapstock.

The following generalities emerge from a consideration of free fatty acid. Some bases, in particular caustic, promote losses by saponification of neutral oil unless used to prevent such a reaction. Soaps entrain oil, and high centrifugal pressure is required to reduce this entrainment. Color is a most discouraging contaminant. So far as can be determined, caustic alone of the inorganic chemicals useful for refining an edible oil will react with the color colloids and render them soluble in water. Since caustic is also a saponifying base, the physical chemistry of soap formation must be carefully viewed.

It is well known by the soap boiler that saponification is hard to start when neutral oils are mixed with caustic but that this proceeds very quickly once soap is present in the mixture. In this respect saponification might be classed as autocatalytic, progressing much faster if soap is already present.

A serious process consideration therefore is to use decolorizing caustic in somewhat meager quantities or to eliminate all soap from the oil before adding excess caustic for this purpose. Several processes have been offered wherein excess caustic has been added with soap present but contact time reduced below the point at which serious damage is done to the oil by the time-consuming reaction of saponification. This usually takes very large caustic dosages, and over-all refining may not always be complete with respect to degumming.

The following generalities emerge from color consideration. Losses due to saponification of neutral oil by decolorizing caustic may be reduced by removing the soap formed by neutralization of the free fatty acids prior to decolorizing. If this is not done, losses will depend on decolorizing caustic treat.

Meal, moisture, and traces of residual soap need not be mentioned. Meal deposits in the centrifuge and moisture are extracted with no loss by vacuum drying. Residual soap is easily washed out of the oil by water with only insignificant losses.

The important concept to be derived from a study of the contaminants existing in crude vegetable oils is that each component may be treated by different means for its own removal. These several steps can be considered separately and practiced in the refinery as a combination of separate steps or as a single, simultaneous grouping of all steps.

Classification of Processes

The caustic process is, of course, the most widely used and best-known refining process. It is based on a single treat of caustic in aqueous solution which supplies water for degumming, caustic for neutralizing the free fatty acids, and excess caustic for decolorizing. Selection of caustic strength, mixing time, mixing energy, temperature, and quantity of excess caustic all play an important part in making this process operate well.

From the principles of the previous section it is obvious that although good color can be obtained by high excess caustic treats, these treats will contribute materially to plant loss. Since temperature is known to advance the rate of saponification of neutral oils, refining temperatures should be kept low. This always increases the oil viscosity, reducing centrifugal separation efficiency. Most oils will not refine well at low temperature although expeller cotton oil is notable for its requirement of low temperature for good refining.

The excess caustic adds materially to the volume of caustic refined soapstock, and here again losses are increased by producing more soap, which in itself entrains more oil.

In spite of these basic problems caustic refining can show excellent results. Close attention to detail is required, but if this is properly executed, loss factors can be controlled within reasonable bounds. True savings of about 20% over average kettle refining are possible with the better results being reported from operations which exert strict control over daily refining through a chemical laboratory or a central engineering office.

The second process offered was the Clayton Soda Ash Process. Neutral oil destruction is essentially eliminated during degumming and neutralizing of FFA by using a refining reagent which does not saponify oils. Sodium carbonate however, when neutralizing FFA, releases CO_2, which tends to hold up in the soap and make it float.

To eliminate this tendency a dehydrator is provided, which draws off all the CO_2 and the moisture from the mixture prior to separation. An additional rehydration treat becomes necessary to produce an insoluble fluid soapstock for centrifugal separation.

Since sodium carbonate will not remove color, a second refining stage is employed wherein decolorizing caustic is added. At this point the gums and soap have been removed, and, as pointed out, the oil can be heavily treated without significant plant loss.

True plant savings over settlement losses of 30 to 35% can easily be obtained on most oils, with savings on degummed soya as high as 55%. The most striking factor recommending this process is its ability to reduce all oils to a common standard before re-refining for color. The quantity of soda ash used to accomplish this almost eliminates differences between oils on primary refining, such that one soda ash Baumé, one formula for treat, and one temperature are sufficient for all but the most unusual oils.

The third process would logically become an extension of the soda ash process. In principle it recognizes that the elimination of CO_2 is not necessary beyond the point at which soap floats. At least two systems are used to accomplish this. Pressure such as is possible in a Hermetic installation can solubilize some of the CO_2 and minimize the problem. A gas vent tank accomplishes the same purpose.

By practicing this procedure, the previously required steps of dehydration and rehydration are eliminated. The process becomes less efficient for high FFA oils, but phenomenal color reduction is possible through the medium of re-refining clean oils.

The fourth process uses a non-saponifying primary reagent ammonia. The main advantage is the ability to boil off all the ammonia from the soapstock, thereby recovering most of the refining reagent and producing a by-product consisting of all the plant loss material. The soapstock is not usable for distillation but is an excellent feed additive for solvent-extracted meal. This fact reduces the areas of application for the process.

The fifth process might be classified under some such generality as "stoichiometric caustic." Primary refining is carried out by the addition of caustic, but in quantities to neutralize the FFA only. This uses up all the caustic added, leaving none for saponifying neutral oils. Additional reagent must be added to grain out the soap. This can be done by adding soda ash after the caustic treat to the oil mixture, or by adding a reagent flush to the centrifuge. This process again has the advantages of separate re-refining and can handle oils up to 30% FFA. Savings of 30% are easily obtained, with most plants reporting up to 35%.

The sixth process is refining in the miscella state. The most popular plant system for miscella refining is straight combined caustic refining although it has been demonstrated that ammonia refining and caustic re-refining are also possible. Obviously it is necessary to carry out miscella refining at such a location that miscella is produced normally. Reconstitution of an oil into a miscella is not feasible either from an economical point of view or from process considerations.

Savings for this process cannot be reported with any accuracy since the oil being refined cannot be classified as crude oil under A.O.C.S. or N.C.P.A. rules. Excellent results have been reported however, based on oil produced per ton of meal.

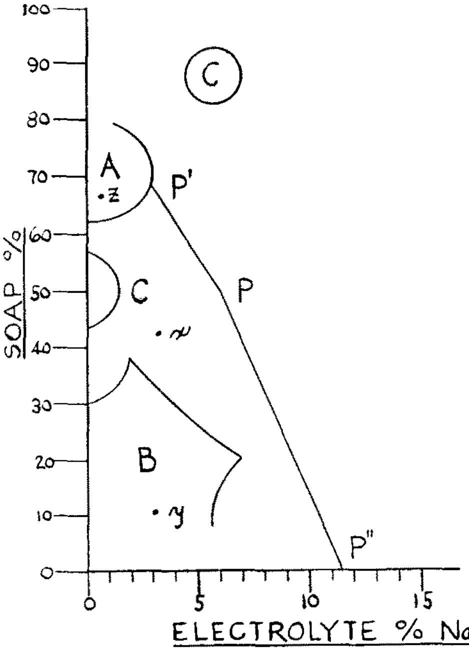
The seventh process is a further separation of refining components. The oil may be separately degummed prior to refining and any of the first six systems practiced. In general, this does not improve savings since gums dissolve rather than entrain oil, but the refining soapstock is much better as a byproduct when used directly in the manufacture of soap.

Physical Chemistry of Refining

Having discussed the source of losses in refining and having briefly outlined some seven process conditions, I can now delve deeper into the physical chemistry of refining and set up some boundary conditions for making any process work.

First may be considered the phase diagram for making soap. This is well known to the soap boiler but rather obscure as applied to vegetable oil refining (Figure 1).

The area marked A represents the boundary conditions for neat soap, a condition of true precipitated soap which could be separated easily in a centrifuge from oil or some other aqueous phase. The area marked B represents the boundary conditions for a nigre phase, a continuous aqueous phase which contains dissolved soap. Areas marked C represent special soap formations which need not concern us here. The diagram is used as follows:



NOTE:
TYPICAL PHASE DIAGRAM FOR COTTONSEED OIL SOAP ONLY. SPECIFIC LOCATION OF POINTS ARE NOT ACCURATE.

FIG. 1.

Analyze a sample of soapstock for sodium soap and for total free electrolyte content. Assume that if this analysis were to show 6% electrolyte as NaOH and 50% sodium soap, the balance of 44% will be water, gums, and dirt. Locate this point, P, on the diagram. It is now possible to determine what conditions exist in soap stock of this analysis by drawing a line such as P^1P^{11}. The exact line drawn is, of course, determined by the necessity that equilibrium conditions be fulfilled. Neat soap containing 68% sodium soap would coexist with an aqueous phase containing 12% electrolyte and no soap. The latter is called a pitch water.

It will be noticed that extension of a line through a point such as x must intersect the boundary conditions of a nigre phase which does contain soap. Under these conditions no fat-free pitch water could exist. Note also that conditions which analyze as points y or z fall wholly within the single phase areas of B or A and only the single condition of nigre (soap solution) or neat soap would exist.

Now let us examine the conditions of refining for the several process types and interpret the soapstock phase in terms of the phase diagram. Perhaps the easiest to understand is the situation when re-refining a neutral oil, as in the soda ash process. The electrolyte content of the treat will be between 10 and 25%. Obviously a line can be drawn between neat soap and the horizontal ordinate indicating two phases, neat soap and pitch water. The oil, of course, represents a third phase, and standard refining centrifuges will discharge only two phases.

It therefore becomes necessary to change these phase conditions. The best method is to inject water into the machine after these two heavy phases have been separated from the oil. This lowers the electrolyte concentration to a value between 2 and 4%. So long as the total soap existing in the re-refining mixture is low, conditions exist for a single phase of soap solution in water of low electrolyte content.

This means that re-refining foots must be below about 6% electrolyte concentration and contain only small quantities of soap for the operation to be carried out at maximum efficiency. Note that this is a single aqueous phase and, as such, can entrain no neutral oil. In other words, plant losses from neutral oil due to proper re-refining should be zero. If three phases exist, surging of the middle phase from the light to the heavy can cause poor oil and periodic excess losses.

It is equally important to undersand that if there is too little electrolyte present (and too much soap), the problem of emulsion between oil and the aqueous phase can become troublesome. As is well known, water washing is subject to these problems when too much soap gets into the oil to be washed. The operator cures this condition by adding some solid sodium chloride, raising the electrolyte concentration of the wash water out of the danger zone. On re-refining, such a condition can occur if process conditions allow soap to spill over from the refining stage or if process conditions are such as to accelerate saponification in the re-refining mixer or heater. This saponification uses up caustic, lowering the electrolyte concentration too far to prevent emulsions.

In respect to the fifth process, this phase diagram helps to interpret primary refining. Assume that a caustic treat is used which can exactly neutralize the FFA but no more. This leaves no excess electrolyte, placing conditions on the extreme left portion of the phase diagram. Depending on how much soap happens to be made by the caustic treat, there could be a very weak electrolyte solution containing a high relative concentration of soap, a two-phase mixture of soap and nigre or a single phase of neat soap. The first two rapidly promote emulsions which lose oil while the third phase of 65 to 80% soap becomes too hard to handle physically.

It therefore becomes necessary to shift the phase conditions by adding electrolyte or an electrolyte solution. The electrolyte solution may be soda ash, caustic, or sodium sulphate and may be added with the oil or injected into the separated soapstock phase as a centrifuge bowl flush. They all accomplish the same purpose.

The conditions are shifted to the right out of the emulsion zone and lowered out of the zone of single-phase neat soap. Two phases of nigre and neat soap are acceptable so long as the electrolyte concentration is not in the emulsion range and so long as enough neat soap is present to absorb the nigre phase in its mass.

If caustic is used, it must be added as a bowl flush to the soap phase only in order to reduce saponification of neutral oil. Sodium sulphate flush is the most popular reagent although recent work makes sodium carbonate addition to the oil mixture quite attractive.

In the same way each process lends itself to such a phase diagram analysis. The excess caustic of the caustic process required to decolorize forunately becomes diluted by water from caustic solution used to neutralize FFA. However enough concentration is usually left over to stay below a pitch-water phase condition but above an emulsifying weak solution.

The full soda ash process required rehydration in order to bring the percentage of soap down to a recognizable position on the diagram.

Examples Selected from United States and Mexico

Recent data from extended, full-scale refinery operations throughout North America will illustrate what can be done by utilizing these process concepts. In most cases the data are based on oils which do not refine easily by the kettle or by the caustic process. It is natural that equipment suppliers should be called in for demonstration test work when problems occur and not on smooth operations.

In Mexico 20 tank cars of dark Expeller cotton oil were refined by the modified soda ash process. The best that could be done by the caustic process was to produce oil which bleached to a 4.7 red while showing a savings of 17% over a settlement loss of 7.6% and a bleach color of the settlement oil of 4.1 red. The modified soda ash process gave oils color as desired between 3.0 and 3.5 red, with an average savings of 24%. Since that time reports indicate a steady improvement in savings as the unskilled operators become more familiar with the process.

Eight batches of mixed cotton oil were refined by the modified soda ash process and by the process involving a stoichiometric treat of caustic with soda ash electrolyte adjustment. Caustic refining of this oil gave a bleach color of 3.5 red and showed a savings of 15% over a settlement loss of 6.0% and a bleach color of the settlement oil of 2.7 red. The soda ash process gave oils down to 2.0 red while showing a savings, which averaged 30%. The same color and savings were attainable with the stoichiometric caustic process.

Two batches of California Expeller oil were refined by the stoichiometric caustic process, using a flush to adjust electrolyte. Savings of 30% were obtained over a cup loss of 8.3%, and the settlement bleach of 4.6 red was reduced to 3.5 red in the plant.

Thirty tank cars of degummed soya were run on the soda ash process. No caustic comparisons were made, but these runs averaged 54% over an average settlement loss of 2.0%.

Data of this type are available from 400 separate runs in The Sharples Demonstration and Research Refinery. They show consistent loss improvement of ½ to 1% for a two-stage refining over a one-stage caustic plant. Color advantage has been exceptionally good compared to caustic or cup.