Fundamental Principles of Refining

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THE following remarks should be understood to apply only to the common alkali refining process, as applied to hydraulic pressed crude cottonseed oil. They are mainly intended to emphasize the more important points brought out in the study of the refining method, made under the direction of the Refining Committee during the past year.

We should first consider the object to be attained. This consists in removing, with the lowest possible loss, those bodies which are not wanted in the product as sold to the ultimate consumer. These are of three general classes: (1) free fatty acids; (2) coloring and resinous matters, together with various other bodies containing phosphorus and nitrogen, all of which are soluble in the oil, or may actually be combined with the glycerides; (3) insoluble matter, such as settlings of meal and moisture.

Generally speaking, the refining procedure consists of two stages:

1. The chemical action between sodium hydroxide and some of those constituents of the crude oil which are to be removed.
2. The conversion of the products formed in the first stage into a form that will separate readily from the refined oil.

We often think of the refining procedure only as a mixing operation, because it is carried out in a mixing apparatus. It is just as important, however, to bear in mind the equally necessary second stage, not a mixing at all, but a separating operation, and this stage should not take on the nature of a mixing operation.

The principal points to be briefly discussed here are:

Choice of lye
Agitation
Temperatures
Separating foots from refined oil
Practical application

Choice of Lye

The sodium hydroxide is necessarily dissolved in water before being applied to the crude oil, for two reasons:

1. To bring it into a condition where it will react chemically.
2. Because water is necessary to dissolve and emulsify the products formed.

The relative amounts of sodium hydroxide and water constitute what we usually speak of as the concentration of the lye. It is found that some oils refine best with strong lye and others with weak lye, even when there is no difference in free fatty acid content. This is at least partly due to the fact that the quantity of impurities present in certain oils requires a lye with more water to form the desired emulsion.

When the F.F.A. in an oil increases, more NaOH is required for neutralization, but the amount of water required does not necessarily increase correspondingly; hence, we generally find stronger lyes best on oils with high F.F.A. On oils of usual average quality, however, it is generally found that lower losses result when relatively weak lyes are used, as less saponification takes place with such lyes.

It is found in practice that if we use only just enough sodium hydroxide to combine with the acidity as found by the usual test for free fatty acids, we will not remove all of the coloring matters. The presence of a very considerable excess of sodium hydroxide throughout the entire refining is necessary for removing all of the undesired impurities. It is found that if, during the process of refining, the excess sodium hydroxide becomes neutralized by saponification, we do not obtain as light a color in the refined oil at the end of the operation as when an excess of sodium hydroxide remains. While, therefore, a certain excess is necessary in order to obtain proper color, an unnecessarily large excess causes increased saponificaion of neutral oil with a resulting increase in loss. A certain amount of such saponification always takes place unavoidably, and due to this and to other complicating factors, it has never been possible to predict or to calculate exactly the proper quantity or strength of lye to give the best quality of refined oil with the lowest loss. At present, this can only be determined by experimental refinings.

The best we have so far been able to do is to set an upper limit for the amount of sodium hydroxide which may safely be used, and specify certain strengths which have been found to give good results on oils of various F.F.A. content.

It is to be hoped that we may eventually know more about the various constituents of crude oil, so that by some test we may determine the quantity present, just as we now determine the F.F.A., and then calculate from these tests the proper amount and strength of lye to use.

Agitation

The first essential in refining is to cause the sodium hydroxide solution and the crude oil to come into very intimate contact, so that every molecule in the oil comes in contact with free sodium hydroxide. As oil and water do not mix naturally, the desired contact can only be attained by extremely vigorous agitation. This intimate contact is especially difficult to attain on oils with high F.F.A., where the large amount of soap formed tends to hinder or obstruct the action of the caustic on the other unacted-on particles. Even with the most vigorous possibe agitation, the element of time is of importance. It is found that the agitation must be continued for a considerable time in all cases, in order to bring the reaction to anything approaching completeness. On the other hand, if such agitation is continued unnecessarily long, excessive saponification of glycerides takes place, resulting in an increased loss with no improvement in the color. Our work shows that agitation at 250 RPM with a paddle having one-inch blades for a period of five minutes is sufficient in most cases, but on some oils ten minutes gives a noticeably better result. Beyond this point our experiments do not show any improvement, but do show an increased loss. Hence, ten minutes has been adopted as the standard time for all oils.

Temperature

The temperature of mixing is of great importance. The above mentioned agitation for ten minutes is based on a temperature of 18-22°C., or approximately 70°F. Our experiments showed that when mixed at lower temperatures, down to 50° F., satisfactory results—both as to color and loss—are obtained, but it is not considered practical to require chemists to operate much below ordinary room temperatures where there is no decided advantage to be obtained. Temperatures of 80° F. or above resulted in darker color or higher loss. Hence, 18-22° C. has been adopted as standard. At ordinary temperatures, the F.F.A. react readily, and apparently the resinous and coloring matters are likewise attacked easily, while the glycerides are not saponified to any great extent. At higher temperatures, saponification of neutral oil takes place much faster.

Separating Foots

At the end of the mixing operation at 18-22°C., we have a mixture of refined oil and finely divided foots, the latter term comprising the soap, coloring matter, and other impurities, together with excess of lye and some emulsified oil. This mixture in its present state of division and temperature will not settle and separate the foots readily. If the mixture be filtered at this stage, the refined oil will be found to have the desired good color, and to this extent the refining operation has accomplished its purpose. It is only necessary then to separate the foots, for which purpose they must be brought into a condition where they will settle readily, and do so without carrying down a large amount of neutral oil. This is accomplished by heating to such a temperature as will cause the small particles to soften and coalesce into larger and heavier masses, at the same time liberating most of the oil originally enclosed or entrained in the small particles. We then find that the foots settle so that the refined oil can be drawn off, leaving only a minimum quantity of neutral oil in the foots. It is impossible to produce a foots containing no neutral oil. The optimum temperature for softening the foots so they will settle readily varies greatly with different oils, and with the relative amount of water present. Crude oil containing only a relatively small amount of impurities, or oil which is refined with a weak lye, will usually make a foots which will soften at a relatively low temperature, and vice versa. The minimum temperature can only be determined by experiment in each case. It has been found, however, that temperatures higher than about 60 or 65°C. frequently give trouble by causing the foots to rise to the top, due apparently to the expansion of air bubbles contained in same, so we have set a maximum limit of 60°C. or about 140°F. If the foots do not settle promptly when this temperature is reached, they will usually do so after being held for a few minutes at this temperature. One of the most essential points developed by our experiments is, that in heating the mixture to soften the foots, it is very important to heat quickly. The former theory of heating slowly resulted in no advantage whatever, but on the contrary has led to extremely variable results; and generally speaking to poorer results, especially as regards loss. The longer time taken in heating can only result in an increased saponification of neutral oil. Hence, we find by experiment that the light color obtained in the cold mixing is preserved and the refining loss kept at a minimum if we heat the sample to the desired final temperature rapidly. Heating beyond the minimum softening temperature up to the beforementioned limit does not injure the refining, provided the sample is not mixed vigorously during this operation. Mixing during heating is unnecessary and undesirable, except to the extent that we keep the mass moving just sufficiently to hold a uniform temperature throughout the mass while heating. A speed of 70 RPM with the 1" paddle has been found sufficient. Additional agitation results only in breaking up the particles of foots or preventing them from properly coalescing so as to settle well.

What we are really trying to do at this stage of the refining operation is to separate two constituents of the mixture, and not to mix them.

Practical Application

This may be considered from the standpoints of both laboratory and factory operation.

For laboratory work, the principles described have been embodied in a revision of the official refining method recommended for adoption by the Refining Committee. It will be necessary to obtain new paddles, and to modify existing refining machines to meet the requirements of two speeds with positive drive, and quick heating. Then it will be necessary for chemists to religiously follow instructions to the letter to obtain results equal to those obtained by others.

In applying these principles to factory work, it is a difficult mechanical problem to obtain the same thoroughness of mixing in a given time on such a large scale, or to heat a large mass of oil to a high temperature as quickly as it can be done on a laboratory sample. Hence, while the same principles should apply, it will probably never be possible to get quite as low losses in a large kettle as in the laboratory.

Report of the Chevreul Prize Committee

By DAVID WESSON

THE Chevreul Prizes are being offered for the three best original articles published in OIL & FAT INDUSTRIES during the season 1926 and 1927.

The judges of the article will be selected from members of the American Chemical Society and the American Institute of Chemical Engineers.

The first prize will be $150.00; the second prize $100.00, and the third prize $50.00.

The Contest closes with the July number of the Journal.

The announcement of the winners will be made at the earliest possible moment.

DAVID WESSON, *Chairman.*