Some Recent Developments in the Refining of Fatty Oils

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Refining is the most important step in the processing of crude fatty oils to prepare the resulting refined oil for such further treatment as is deemed necessary for the particular use intended. The opportunity for making the most dollar savings is in refining operation. Bleaching, hydrogenation, winterizing, and deodorization are all indeed important, but they are techniques wherein the losses of oil are nominal, restricted, and small compared with those incurred in the refining step or steps. The margin in pounds of refined oil available for saving through efficient refining per tank car becomes greater as the free fatty acid and Wesson Loss of the crude oil increase.

After the replacement of batch by continuous refining with caustic soda, the next phase in the development was the substitution of sodium carbonate or soda ash, a nonsaponifying alkali, for caustic soda, with the primary intent of eliminating the saponification of oil that resulted from the reaction with the latter alkali.

Neutralization of the free fatty acids of the crude oil using soda ash however, meant having carbon dioxide, a gas, as one of the products of the reaction. Unless means were provided for taking care of the carbon dioxide through physical or chemical expedients, it could interfere with efficient operation or perhaps render the refining operation impractical. There were two approaches to the problem.

One was to add a large excess of soda ash to form the bicarbonate to avoid the evolution of appreciable carbon dioxide (1). The soda ash required for 2.5 times the amount necessary to neutralize the free fatty acids represents a sizable quantity in terms of pounds of alkali per tank car of oil refined and constitutes a burden in cost when the free fatty acids of the crude oil are high.

The other approach was to add the soda ash in moderate excess, 1¼ to 1½ times the amount necessary to neutralize the free fatty acids and to remove the carbon dioxide with most of the water in a dehydrator. The soapstock was rehydrated with soda ash solution. The soapstock-oil mixture fed to the centrifuge was in an essentially nonemulsified condition, a mixture that was readily separated into a clear oil effluent with less than 0.05% free fatty acid and a soapstock very low in free oil, 5.0 to 10.0%, dry basis. Having removed the gums and free fatty acids, the oil was then re-refined with caustic soda (2).

To obtain the maximum reduction in color and other residual impurities, it was found necessary to use concentration of caustic soda of 20°Bé. and higher. When this was done however, the separation of the phases was not clean, *i.e.*, the soap was grained out by the strong caustic and formed an intermediate layer between the oil and nigre, which interfered with a sharp, two-phase separation into clear oil and a soapstock without emulsified oil. To solve this problem, a water flush to the centrifuge was devised whereby the water diluted the soapstock to form a single phase in which the soap was dissolved (3).

The dehydration-rehydration soda ash-refining process gives very high yields of refined oils. However reducing the cost of chemicals when refining medium and high free fatty acids crude oils and simplification of the equipment with the elimination of the dehydration step was desirable.

Caustic Soda-Soda Ash Refining, the CSA Process

The CSA Process was developed as an extension of the soda ash processes to expand their applicability to very high free fatty acids crude oils and to reduce the consumption of chemicals (4).

The advantages of having a nonsaponifying alkali were apparent in the soda ash processes. It was then reasoned that there would be no loss of triglycerides through saponification if caustic soda in amounts just to neutralize the free fatty acids of the crude oil were used, provided the mixing of the caustic soda with the oil gave a rapid, uniform dispersion of the alkali in the oil. This meant having an accurate reliable proportioner and a suitable, efficient mixer. A positive displacement proportioning pump (5) and a pipe line mixer (6) were developed to meet the requirements in the CSA Process for accurate proportioning and efficient mixing to obtain the maximum yields. Both of these units of equipment have been in operation in plants and have given very satisfactory results. One mixer has served for mixing the caustic soda solution and the other for the soda ash solution in an eight-tank car-a-day capacity CSA oil-refining unit.

The rationale of the CSA Process is to neutralize the free fatty acids of the crude oil with strong caustic soda solution, employing approximately just enough to neutralize the free fatty acids. The use of strong caustic solution is for the purpose of keeping the soapstock volume at a minimum. After the caustic soda solution has been uniformly and rapidly dispersed in and mixed with the oil, the mixture has added to it a small amount of soda ash solution to precipitate the soapstock. The soda ash also acts as a means of ensuring the completion of the neutralization without danger of either saponification of oil or evolution of carbon dioxide. The amount of soda ash solution (20°Bé.) varies from 1.5 to 4.0% for crude oils of 1.5% to 6.0–8.0% free fatty acids.

The initial caustic soda treatment imparts a "slip" to the resulting soapstock compared with soda ash soapstock, which, for medium and high free fatty acids crude oils, requires relatively large quantities of soda ash solution to be used in the refining to increase the moisture to 45% and higher to have soapstocks that the centrifuges can discharge continuously for prolonged periods.

The caustic soda solution is usually 30–32°Bé. although higher concentrations are feasible. There is one caustic supply tank which serves the neutralization and the re-refining steps. Caustic soda of 30–32°Bé. is more than adequate for the reduction of difficult-to-bleach cottonseed oils.

Inasmuch as the percentage of caustic soda solution added is critical in the CSA Process, it is sound practice to check the delivery of the proportioner, for which the pH titration method is recommended (7).

The temperature conditions for CSA refining are essentially the same as in the soda ash refining processes except that the crude oil is at 100–110°F. when the caustic soda solution is added to it. The temperature of the mixture entering the primary centrifuge is 195–210°F.

The CSA Process has not only shown to advantage in the refining of high free fatty acids crude oils but is superior to the Modified Soda Ash Process for the refining of crude cottonseed oil, free fatty acids 1.8% (8).

A carefully conducted series of tests was made in which the CSA and the Modified Soda Ash Process of refining were compared. Three million pounds of crude cottonseed oils were collected in a storage tank and kept under continuous circulation for several days before test time. The free fatty acids of the composited mixed crude oil was 1.8%, the cup refining loss 7.7%. The CSA Process, carried out essentially as described, gave a plant refining loss of 35.7% lower than the cup loss while the Modified Soda Ash Process, in which 2½ times soda ash solution (22°Bé.) to neutralize the free fatty acids was mixed with the crude oil, showed a plant refining loss of 26.4% lower than the cup loss. The mixture of oil and soda ash solution went through heat exchangers and a vent tank before going to the Sharples centrifugals, which were also used in the CSA test. The same re-refining procedure and equipment were used in both processes. The reagent was 1.5% of 30°Bé. caustic. A flush of water in the re-refine centrifugals was employed.

The results of the comparative tests on this eight-tank car-a-day unit were so convincing that the refinery adopted the CSA Process, which has since been in exclusive use for cottonseed oil. The soapstocks from the CSA had 37.0% moisture and 40.0% T.F.A. while the Modified Soda Ash soapstocks had 45.0% moisture and 30.0% T.F.A. The 40.0% T.F.A. puts the CSA soapstocks in the merchantable class.

The CSA Process for crude cottonseed oils, free fatty acids 4.0 to 8.0%, has given refining losses 25.0 to 35.0% lower than the cup refining losses, which have ranged from 15.0 to 27.0%. In these instances the soapstocks had more than 50.0% T.F.A.

To convert a soda ash process, one that does not include dehydration, to the CSA Process, involves the addition of an accurate proportioner, a suitable, efficient mixer, and a U-shaped pipe, 8 to 10 in. in diameter and approximately 6 ft. long, which acts as a hold-up chamber for the caustic soda and crude oil mixture before the soda ash solution is admixed. The conversion of a caustic soda refining unit would require the same additions plus a re-refine step.

In summary, the CSA is a flexible process that is adaptable to the widest range of crude oil, from below 1.8% free fatty acids to upwards of 4 to 8% free fatty acids, as high as is normally met in practice. It offers the refiner a scientific approach to refining whereby with the proper equipment he can accomplish an efficient control of the quality of the refined oil and the composition of the soapstocks even when the crude oils may vary widely in free fatty acids and minor constituents.

Refining with Ammonium Hydroxide

A second development of interest is the ammonium hydroxide process. Ammonium hydroxide is a nonsaponifying alkali that is volatile, *i.e.*, it can be removed by heating. Ammonia is given off as a gas. These characteristics are taken advantage of in the Clayton Process of refining fatty oils with ammonium hydroxide to produce a neutralized oil on the one hand and a lecithin product on the other (9). Degumming a crude oil with water yields a lecithin product, but the degummed oil is a crude oil with practically all of the free fatty acids in the nondegummed crude oil.

Refining with ammonium hydroxide eliminates acidulation of soapstock, which at best is a troublesome operation and indeed a nuisance. Moreover it is wasteful because the phosphatides, a valuable source of choline, inositol, etc., are decomposed and destroyed in acidulation. Crude soya oils, the extracted crude soya oils, have 1.5 to 2.5% gums or phosphatides. With 1.5% gums the waste or destruction amounts to 900 lbs. of material per tank car of oil refined. The greater part of this material goes into the acid water where the choline, inositol, and other products of the splitting of the gums, which are stimulants and supporters of bacterial growth, increase the biochemical oxygen demand and thus aggravate the sewage disposal problem. It is not sound practice, now that the benefits of adding phosphatides to meal, particularly extracted meal, and to feed concentrates, are recognized, to leave these compounds in the crude oil and then have them destroyed in subsequent refining of the oil and acidulation of the soapstock.

Refining with ammonium hydroxide as distinguished from degumming removes from the crude oil the free fatty acids as well as the gums, thereby attaining the maximum yields of a lecithin product that has the indigenous free fatty acids for incorporation with meal.

In refining with ammonium hydroxide, crude soya oil, preheated to 130–150°F., is mixed with 1.5–2.5% of 5 to 14% NH_3 solution, and the mixture is sent through a mixer and coil or heat exchanger (total residence time about 5 to 15 min.) and then to a closed centrifuge, preferably one of the pressure type, because ammonia fumes must not escape to the atmosphere.

A dried lecithin product from a typical ammonium hydroxide refining of a nondegummed crude soya oil has approximately 30 to 33% acetone-solubles of which one-fourth to one-third is free fatty acids. The amount of fatty acids (free fatty acids) in the acetone-solubles depends, among other factors, on the free fatty acids of the crude oil. Dried ammonia lecithin products with acetone-solubles as low as 22% have been produced.

Ammonium hydroxide removes more color bodies than water but less than soda ash or caustic soda. For example, the carotinoid content of the lecithin from ammonium hydroxide refining of a crude soya oil was usually 1½ to 2 times that of the lecithin from the water degumming of the same crude oil. Concentrations of carotinoid as high as 0.035%, dry basis, in the ammonia lecithin product have been produced.

The ammonia gums as discharged from the centrifuge are softer than water gums of approximately the same acetone-solubles, dry basis, content. As a result, lower pressures are required in the separation of the former than of the latter in the centrifuge.

With the trend towards solvent extraction for producing crude fatty oils other than soya oil, the advantages of refining with ammonia hydroxide can be realized for the former. Crude corn oil, from prepressing and solvent extraction, normally has 2.0 to 3.0% free fatty acids and 1.5% to 2.0% gums, most of which are phosphatidic in nature. Whether refined by the caustic soda or soda ash process, the resulting soapstock is usually acidulated. The glycosides in the gum complex are very powerful emulsifiers that are not easily split by the acid under the conditions of acidulation. These compounds tend to concentrate in the interface and contribute to the stability of the emulsions. The nutritive phosphatides present in the crude oil are decomposed in the acidulation of the soapstocks and end up in the acid water that is sewered.

An ammonium hydroxide refining of a crude corn oil (free fatty acids 2.6%, 1.72% phosphatides [% P × 26]) was made in the pilot plant. The crude oil, preheated to 130°F., and pumped at a rate of 1.0 g.p.m., was mixed with 2.9% of 10% NH_3 solution delivered by the piston proportioner; the mixture went through a mixing zone, mechanical mixer, and a coil before entering a Modified Podbielniak Contactor (see infra).

The oil effluent from the Contactor was clear, and the soapstock or gums discharged as a soft flowing mass. The pressure of the mixture into the Contactor was low, 37 to 40 p.s.i. The dried soapstock is a lecithin product that was fluid when warm and assayed 32.0% each of free oil and free fatty acids. The ammonia-refined corn oil had 0.15% free fatty acids and 0.0050% P. Laboratory deodorization of the washed, dried oil gave a deodorized oil that had a good odor and taste.

The ammonium hydroxide-refined, water-washed, dried soya oil had 0.04% free fatty acids and was heat-break free. Deodorization of the oil under conventional commercial practice yielded an oil that was stable and had an exceptionally good flavor.

A four-tank car-a-day capacity ammonium hydroxide refining unit has been in operation for more than six months in a Midwest soybean extraction plant, Iowa Soya Company, Redfield, Ia. The advantages of the process have been realized. It is believed that the industry will soon recognize the desirable properties and merits of the oil that is capable of being produced by this process.

Simultaneous Separation of Soapstock and Washing with Water

In the present practice of the continuous refining of fatty oils, a separate water-washing step follows the refining step or steps, that is to say, there is a refining step or steps in which the crude oil is treated with an alkali or other reagent and the soapstock is separated from the oil in a centrifuge. Then in a succeeding step the refined oil is washed with water and the wash water is separated from the washed oil in another centrifuge.

The third process discussed is the development of a commercial process in which the caustic refining and the water-washing steps are combined, with the separation of the soapstock from the oil and the water washing of the oil in one centrifuge.

The importance of size as well as the avoiding of emulsification within the centrifuge, particularly in the areas where the water is introduced and the soapstock is separated, was established.

The Podbielniak Contactor with its large-diameter rotor has given encouraging results after it was modified for a process of merging into one step the two steps of refining and water washing (10).

Pilot-plant tests were made to prove the efficacy of the process. The Modified Podbielniak Contactor served as the centrifuge in which the soapstock was separated from the oil and the oil was washed with water. A degummed crude soya oil (free fatty acids 0.35%) was refined with 1.5% 20°Bé. caustic soda. The oil, preheated to 125–130°F. and pumped at a rate of 1.0 g.p.m. from a supply tank was mixed with the caustic soda solution added by the piston proportioner. The oil and caustic went through a mixing zone, a vertical mixer equipped with paddles, and through a coil, temperature 150°F., and into the Modified Podbielniak Contactor, a Kates valve controlling the amount of water, which was varied from 10 to 17%. The oil effluent was clear, moisture 0.22%, and the soap content, determined by the flame photometer method, was down to 80 p.p.m. The soapstock was a clear yellow liquid that assayed 4.2 to 6.0% T.F.A., depending on the countercurrent water rate, and was practically free of occluded or emulsified oil. The calculated refining loss was 0.75%.

Maintaining the pressure differential low between the mix going into and the oil coming out of the Modified Podbielniak Contactor resulted in a very clear oil effluent, 0.25% moisture. Carefully controlled differentials of 1 to 2 lbs. have been used with beneficial effects on the clarification of the oil.

Kaiser and Doyle (11) presented and discussed some operating data and results of analysis of the oil effluents and soapstocks from the pilot-plant refining tests.

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