Use of the Centrifugal Contactor for Water-Washing of Refined Oils

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CRUDE VEGETABLE FATS AND OILS contain variable amounts of nonglyceride impurities which are mainly free fatty acids. These impurities are objectionable because they render the oil dark-colored, cause it to foam, smoke, or precipitate gums when the oil is heated during subsequent deodorizing. The object of alkali refining, of water washing, and of activated clay bleaching is to remove the objectionable impurities in the oil with the least possible damage to the triglycerides.

Methods of refining crude oils are a) treating the crude oil with a caustic solution, followed by water washing; b) a soda ash neutralization of fatty acids, followed by a caustic solution to remove color, and a water wash operation to remove the dissolved soap; c) treating crude soybean oil with acetic anhydride, followed by water washing; d) acid or water washing of inedible oils completely to remove material which would precipitate when the oil is heated.

Alkali refining effects an almost complete removal of free fatty acids by conversion to oil-insoluble soaps. Batch or kettle refining consists of placing crude oil and caustic in an open tank or kettle. Caustic reacts with impurities, and heat is added to separate oil and soap into two phases. After the desired degree of ''break'' is obtained, the soap stock is allowed to settle by gravity. The refined oil, after it is drawn off, contains suspended water and soap which must be removed before further processing. Filtration of refined oil through spent bleaching presses will reduce the soap and moisture content. However many refiners who pre-bleach before hydrogenation find that even two such filtrations will not effect complete removal of soap. Excessive amounts of dissolved soap in refined oil make it impossible for the refiner to make a quality finished-product. Soap left in the refined oil will poison nickel catalysts, changing the selectivity of the hydrogenation process, and will cause foaming and color reversion. Soap can form complex iron compounds which are deleterious to flavor, odor, and stability of the finished product. Removal of soap from refined oil is as important as removal of fatty acids from crude oil.

Development of a continuous, centrifugal, caustic refining process has improved refining efficiency and enabled the industry to produce a higher quality of refined oil. The continuous refining process employs centrifugal force to speed up the separation of soap from the refined oil. After centrifugal separation the refined oil still contains moisture and dissolved soap. The dissolved soap is partially removed by a second-step operation. Figure 1 illustrates water washing of the refined oil by addition of 10% by weight of water which dissolves the oil-insoluble soaps and forms a second phase. The water phase containing soap can be centrifugally separated from the oil phase. However the oil phase will retain dissolved moisture which contains soap. Water is soluble in oil in an amount determined by the temperature of the mixture. Oil at 150°F., discharging from the secondary centrifuge, will contain 0.5 to 0.7% moisture, which is actually a soap solution. Subsequent vacuum-drying will remove the moisture, leaving the oil contaminated with a small amount of soap. Over-all plant efficiency and finished-product quality can be improved by complete removal of this dissolved soap.

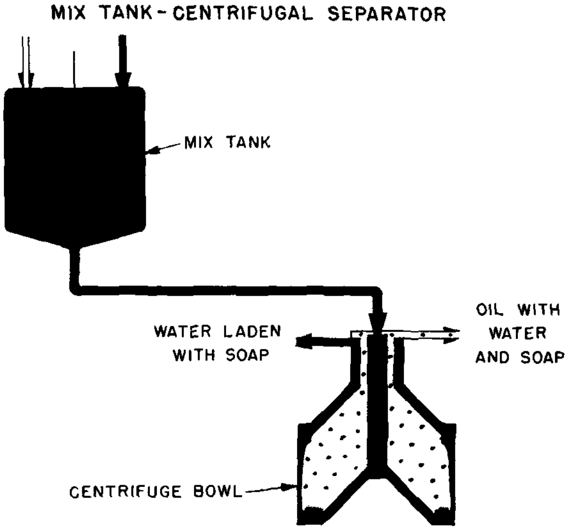

FIG. 1.

Extraction Equipment

Removal of small amounts of dissolved substances by contact with highly selective solvents, such as the removal of the dissolved soap in alkali-refined oil by contact with water, is generally known as liquid-liquid solvent extraction. The various types of equipment for liquid-liquid solvent extraction may be classified into two main categories.

Figure 2 illustrates equipment which provides discrete stages when the liquids are mixed and the immiscible phases are settled and separately removed. The immiscible phases are in equilibrium, and a single mixing and settling operation represents one stage of extraction. The light liquid enters at the right side of the extraction train and travels to the left, countercurrently contacting the heavy liquid entering at the left. The heavy liquid and light liquid are mixed in each stage, and sufficient time is allowed to permit gravity separation in each stage.

Figure 3 illustrates equipment which provides continuous countercurrent contact between the immiscible phases and, in addition, provides phase separation with many theoretical stages of extraction built into a single piece of equipment. An example is a counter-

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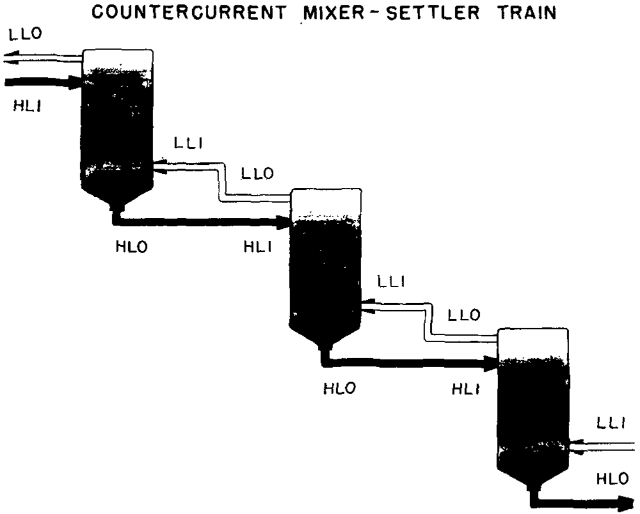

FIG. 2.

current gravity type of solvent-extraction column of simple design. The heavy liquid enters at the top, the light liquid at the bottom. Countercurrent contact is attained by column packing or contact elements. Light liquid is removed from the top of the column, heavy liquid from the bottom. Efficiency is expressed by H.E.T.S., or height equivalent to a theoretical stage.

Gravity extraction-systems can be used for liquids *without emulsion tendencies and with a large specific* gravity differential. The capacity of the column depends upon the diameter. The number of theoretical stages as noted by H.E.T.S. depends upon the density differential, settling rate, emulsion tendencies, and the column packing. A rotating disc column is shown for comparison. The RDC uses energy for contact and provides an H.E.T.S. of one-half that of a gravity column. One gravity separation still limits the use of the RDC to nonemulsion-forming systems.

The Centrifugal Contactor

The centrifugal contactor may be visualized as a gravity type of solvent-extraction tower wrapped around an axis and rotated to create centrifugal force. Figure 4 shows a cut-away view of the contactor and illustrates the flow of liquids. Centrifugal force is utilized in mixing and separating the two immiscible phases. The Hydrazon is a centrifugal extractor designed specifically for the vegetable oil refining process. It consists essentially of a horizontally placed, totally enclosed rotor mounted on a shaft with heavy-duty ball bearings. Inside the rotor are many contacting elements with mixing orifices designed for intimate mixing with low liquid velocities. A calming zone to complete the phase separation is provided for heavy liquid and light liquid before discharge. The heavy liquid and light liquid are kept separate by pressure-balanced, mechanical seals, two on each side of the rotor.

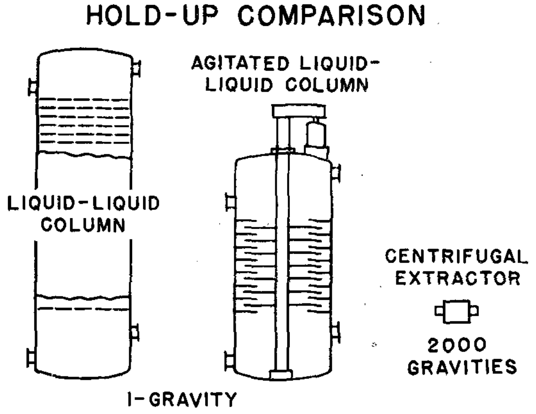

FIG. 3.

The light liquid enters through the shaft and is directed to the periphery of the rotor where it enters the rotor proper. The heavy liquid entering through the shaft at the opposite side is directed to the center of the rotor where it enters the rotor proper. Centrifugal force moves the heavy liquid outward, and, in passing through the mixing orifices, it is intimately contacted with the light liquid, which is pumped into the rotor against centrifugal force. The light-liquid inlet pressure depends upon the radius of inlet, rotor speed, and specific gravity differential of the two immiscible liquids. Contact elements provide for stagewise phase separations. The heavy liquid collected at the periphery moves through a return tube to the shaft and is discharged. A back-pressure regulator automatically maintains a pressure on the light liquid attempting to leave. The effect of this pressure is to control the position of the inter-face separating light and heavy liquids. Back pressure control can be used to control hold-up of either phase in the rotor. For example, a solvent system of 10 parts light liquid, one part heavy liquid would operate with a relatively low back-pressure as compared to inlet pressure. The rotor would be substantially full of the low-flow liquid requiring all of the light liquid to move through the low-rate phase, thus permitting intimate contact between the solvent and the solute.

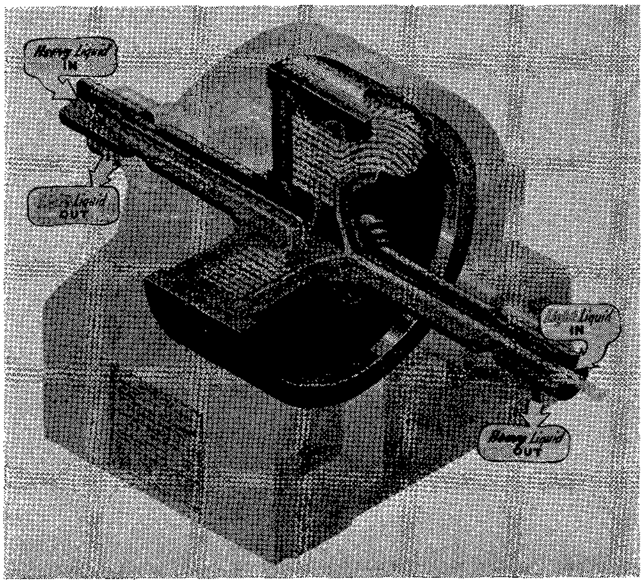

FIG. 4. Diagram showing flow of fluids through a solids-handling centrifugal contactor.

The centrifugal contactor may be compared to a gravity, solvent-extraction column. Capacity of the contactor is increased by widening the rotor. Efficiency of extraction is increased by greater diameters

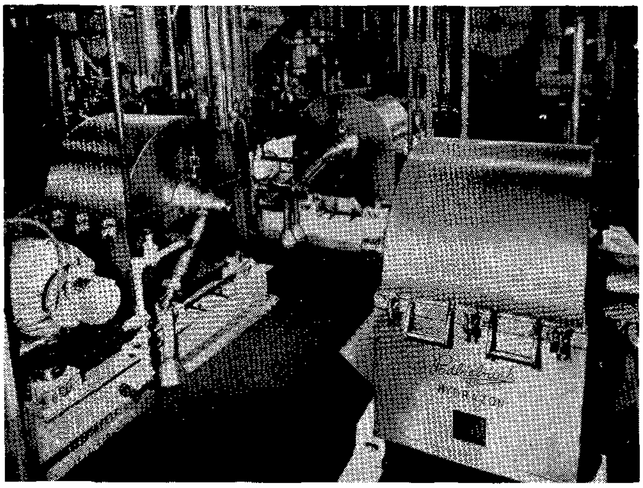

FIG. 5. Vegetable oil refining installation of four Podbielniak contactors.

expressed in terms of radial distance equivalent to a theoretical stage (R.D.E.T.S.). The inter-face position is controlled by back pressure on light-liquid discharge. Similar controls are used on gravity columns.

Flow Sheet

Alkali-refined oil is water-washed in the Hydrazon Contactor by pumping the light liquid against 10 to 15% by weight of water. Intimate mixing is accomplished by passage through mixing orifices, and separation takes place on each contacting element. External mix tanks necessary with centrifuge installations are completely eliminated. Refined oil leaving the Hydrazon is countercurrently contacted with fresh water, insuring that the dissolved moisture in the refined oil going to the vacuum dryer is pure water.

The design and operational procedures have been proven by a production-size unit, parallel to an existing centrifuge installation and the comparing of finished products.

Plant Operation

In February of 1956 the A. E. Staley Company of Decatur, Ill., installed the new 50 Oil Process for refining soybean oil, using the Duozon for degumming and the Hydrazon for water washing of the degummed oil. A Model 6150 countercurrent contactor was used on pilot-plant evaluation of this process. Several months' time was spent in evaluating the use of the contactor for both degumming and water-washing applications. Figure 5 shows the Hydrazons installed in the Staley plant. Each contactor has a capacity of 10 tank cars per 24 hrs. Many advantages have been demonstrated by this installation. The Hydrazon is operated under pressure, which prevents contact of hot oil and air. The installation is completely automatic. The most important advantage, in addition to the replacement of 20 outdated centrifuges, is the operating cycle of the Hydrazon. Daily cleaning is not necessary. The Hydrazon is not dismantled in the field. Low gravities and large coalescing surface provide maximum phase separation without buildup of solid material in the rotor. These machines have operated 24 hrs. a day, 7 days a week, for six months without cleaning.

Hydrazons during the past three years have been operated as water washers on the following caustic-refined oils: refined soya oil, degummed refined soya oil, refined cottonseed oil, refined peanut oil, refined linseed oil, refined coconut oil, tallow, and lard.

Coconut oil is easily water-washed in a Hydrazon because pressure operation keeps out emulsion-forming air. Table I is a condensation of data obtained on actual production tests.

TABLE I

Typical Data Obtained by Water Washing Caustic Refined Oils with Hydrazon

(Model 9700 Hydrazon—36″ diameter capacity—10 tank cars/24 hrs.)

Type of oil	Pressure, p.s.i.g.			Rotor speed	Water	Residual soap
	Oil inlet	Oil outlet	Oil diff.			
				r.p.m.	%	*p.p.m.*
Degummed soya	54	36	18	2,100	10.0	12
Soya	56	40	16	2,100	11.0	8
Cotton seed	65	50	15	2,100	9.8	5
Coconut	75	50	25	2,100	12.0	14

Dissolved soap in refined oil is difficult to determine, especially in amounts below 100 p.p.m. Many different analytical procedures are used in industry, and new procedures are being investigated by a committee of the American Oil Chemists' Society.

The limitations of this analysis are recognized and partially overcome by comparing results of batch and centrifugal water-washing with results of countercurrent water extraction of dissolved soap. The following analytical procedure was used:

Soap Analysis

Reagents: Acetone W/2% H_2O, 0.01 N.HCL, bromophenol blue indicator.

Method: Measure 100 ml. of acetone-water, mix into 1,000-ml. Erlenmeyer, and add several drops of bromophenol blue indicator. Neutralize to yellow end-point with 0.01 N.HCL. Add 100 g. of fat to above solution. A blue or green color indicates soap. Titrate to yellow end-point with 0.01 N.HCL.

Calculations: P.p.m. soap as sodium oleate; p.p.m. = ml. titration × 30.44.

Indicator: 0.1 g. of bromophenol blue, grind with 0.15 ml. NaOH solution (1.5 ml. 0.1 N. NaOH, make to 100 ml. with H_2O) make to 100 ml. with H_2O.

Water-washed oil produced by acetic anhydride degumming was analyzed for residual acetic acid by following analytical procedure:

> Mix 100 g. of refined oil and 100 g. of distilled water, shake in a separatory funnel for one minute. Filter 50 cc. of water layer and titrate with N/4 NaOH, using phenolphthalein indicator. Percentage of acidity is reported as oleic acid.

Solvent extractors were designed to process flammable solvents and are used in many petroleum refineries, chemical plants, and hydrogen-peroxide processing plants. Water washing of miscella-refined vegetable oil, using mix tanks and centrifuges which are not vapor-tight, require extreme precautionary measures to prevent possible explosions. A solvent extractor, Model 6150, has been installed and operated on a portion of the miscella plant stream at the Ranchers Cotton Oil Company, Fresno, Calif. Experimental data on countercurrent water washing of miscella are shown in Table II.

TABLE II
Typical Data—Miscella Refining Process—Ranchers Cotton Oil Company
(Model 6150 extractor)

Pressure, p.s.i.g.		Flow rate	Rotor speed	T.f.a. water out	Soap in oil
Oil inlet	Oil outlet				
		g.p.m.	*r.p.m.*	*%*	
140	90	3	3,000	.009	Trace
140	105	3	3,000	.02	Trace
140	90	3	3,000	.02	6 p.p.m.
125	20	1	2,850	....	1 p.p.m.
122	50	1⅔	2,850	.003	2 p.p.m.
125	56	6	2,850	.007	2 p.p.m.
125	73	7½	2,850	.002	2 p.p.m.
140	123	4⅕	2,850	.02	1 p.p.m.

The purpose of this installation was to demonstrate the advantages to be obtained by countercurrent water washing of miscella, using the countercurrent multistage contactor. Advantages proved during this installation were these: Entire extractor installation is explosion-proof. Waste water did not contain hexane; water could be discharged direct to the sewer system. Refined oil color was improved from ½ to 1 Lovibond red. Extractor has wide latitude of capacity for this operation.

Summary

This paper has discussed the early methods of the refining of vegetable oil and present-day continuous refining equipment. The purpose was to report on the advantages of the centrifugal contactor for water washing of vegetable oil. There are important advantages to be obtained by the use of Podbielniak Rotating Contactor for water washing of alkali-refined oils. One-to-ten tank car capacity with one centrifugal contactor results in space and installation savings. Stainless steel construction permits use of acid treats. Pressure operation prevents oxidation of hot oil and emulsions formed by mixing with air. Installation can be made fully automatic. Periodic cleaning is not required. Countercurrent flow produces higher quality refined oil with 50% lower neutral oil loss in wash water.

Acknowledgments

Special acknowledgment is made to George Cavanagh, Ranchers Cotton Oil, and Noel Myers, A. E. Staley Company, for assistance in supplying data obtained in their plants.

[Received June 13, 1957]

Tallow Alcohol Sulfates. Properties in Relation to Chemical Modification[1]

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THE PRINCIPAL COMPONENTS of saturated tallow alcohol sulfates, sodium hexadecyl sulfate, and sodium octadecyl sulfate are excellent detergents at higher washing temperatures (e.g., 60°) but are less generally useful as surface-active agents at lower temperatures because of limited solubility in water.

Reports from this laboratory in the past few years have shown that the solubility of tallow alcohol sulfates is increased by blending with other detergents (14), also by methods which alter properties as a result of changes in chemical composition.

Thus tallow alcohols retaining the original unsaturation, sulfated with special sulfating agents which do not affect the double bond, result in the presence of the readily soluble sodium oleyl sulfate as a major component (17). Low-temperature additive chlorination at the double bond and sulfation under more usual conditions has a similar effect, producing the readily soluble sodium 9,10-dichlorooctadecyl sulfate as a major component (18). Reaction of ethylene oxide with tallow alcohols and subsequent sulfation also results in improved solubility (1). Another method included in the present report is the formation of the more soluble triethanolammonium salt instead of the sodium salt.

Properties other than solubility are affected by these changes in chemical composition. The present report concerns the detergent and surface-active characteristics of the individual compounds involved, measured under the same conditions, with particular reference to the effect of chemical structure on fundamental solution properties, such as the critical micelle concentration (c.m.c.) and the Krafft point.

Tallow Alcohol Sulfates and Related Compounds

Sodium alkyl, alkenyl, and dichloroalkyl sulfates were prepared as described in previous publications (15, 17, 18): sodium oleyl and elaidyl sulfates by sulfation with pyridine-sulfur trioxide (17), and sodium 9,10-dichlorooctadecyl sulfate from oleyl alcohol by chlorination and subsequent sulfation (18).

Individual ether alcohols of the hexadecyl and octadecyl series, prepared from the alkyl bromide, sodium, and the appropriate glycol (20), were sulfated (16) to give eight compounds of the general formula $R(OC_2H_4)_iOSO_3Na$ where $R = C_{16}H_{33}$ or $C_{18}H_{37}$ and $i = 1, 2, 3, 4$. These compounds are comparable to sulfated ethenoxylated tallow alcohols (1), $R(OC_2H_4)_n$-OSO_3Na, where n is the average number of moles of ethylene oxide condensed. Since they are chemical individuals rather than a mixture of homologs, they more clearly illustrate the relation between chemical composition and properties. The sodium salts of the ether alcohol sulfates did not have very definite melt-

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[1] Presented at the fall meeting, American Oil Chemists' Society, Chicago, Ill., October 20–22, 1958.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.