Continuous Removal of Metallic Ions From Soybean Oil[1]

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ABSTRACT

Removal of metallic ions like copper, nickel and sodium from vegetable oils is important to edible oil processors. Continuous washing of soybean oil with acidic water, followed by ion exchange treatment of the aqueous solution to remove metallic cations and permit reuse of the water, is an effective and economical method for metal removal. Several types of washing apparatus were studied: A Podbielniak countercurrent centrifugal contactor, a rotating disc countercurrent contactor and a contactor-centrifuge system. Equipment for the third system is already available for the continuous washing of refined oil in modern refineries. With a contactor-centrifuge ion-exchange system, copper in soybean oil was reduced by washing from 1.5 to 0.03 ppm; nickel, from 0.4 to 0.04 ppm; sodium, from 20 to <1 ppm. The effects of pH and type of acid (anion) were studied. The cost of washing soybean oil by this method is estimated to be about 0.06 cent/lb, and there is no loss of oil.

INTRODUCTION

A previous report (1) describes a continuous method for washing alkali-refined soybean oil to remove sodium (soap). In this method the wash water, which becomes slightly acidic after treatment with a cation exchange resin to remove sodium ions, is reused. A study of this water recycle washing method has been extended to investigate factors affecting the removal of sodium and other metallic cations from soybean oil; the relation of water pH and other variables to cation removal from the oil; and equipment design considerations.

Advantages of the water recycle washing method include: (a) no effluent wash water to create a waste disposal and pollution problem, except for the small amount of water used during periodic regeneration of the cation exchange resin; (b) effective removal of metallic cations, such as sodium, copper and nickel ions from soybean oil; (c) low cost; and (d) ease of regulating the pH of the slightly acidic wash water.

The need for eliminating the discharge of wash water containing emulsified oil and other biochemical oxygen demand (BOD) material is well recognized today. Effective removal of metallic cations from soybean oil improves edible oil quality since some cations can impart off-flavors, poor oxidative stability, or both (2), to soybean oil. Metal deactivators diminish but do not entirely remove the effects of certain metals. According to our estimates, the cost of removing metals by the recycle washing method is substantially lower than the cost of bleaching, as now used extensively by the soybean processor to remove metals. The effectiveness of washing oil with water to which acid has been added is known (3), but continual control of the pH at a level where corrosion does not become a problem is difficult. With the recycle method of washing the oil, the pH of the water remains substantially constant at a desired level without the further addition of acid except for resin regeneration.

EXPERIMENTAL PROCEDURE

The water recycle system for washing soybean oil to remove metal cations is shown schematically in Figure 1, a simplified flowsheet. Three types of mixing and washing contactors have been used in pilot-scale tests: A countercurrent centrifugal contactor (Podbielniak contactor, Pup Model), a rotating disc countercurrent contactor and a contactor-centrifuge system.

The rotating disc contactor was constructed from a vertical length of 6 ft long X 4 in. i.d. glass pipe. Stainless steel flange plates bolted to each end of the pipe supported a 1/4 in. revolving stainless steel shaft placed axially. Four 3 in. diameter discs made from 1/4 in. thick Teflon were affixed at equal intervals on the shaft, which was driven by a variable speed motor. Two 1/4 in. stainless steel tubes placed along the inner wall of the glass pipe and connected to a steam line heated the contents of the pipe. After recycle water and oil had each been preheated to about 95 C, recycle water was pumped into the top of the contactor and oil at the bottom to give continuous countercurrent flow. The oil-water interface was held just below the bottom mixing disc, the oil layer thus occupying the upper 5/6 of the column and serving as the continuous phase. Results were poor when water was the continuous phase. With the discs rotating at 400 to 550 rpm, good mixing was obtained between the oil phase and water droplets in the immediate area of each disc, and good separation of the two phases occurred in the zones between discs.

The contactor in the contactor-centrifuge combination consisted of six 1 3/4 in. diameter Teflon discs mounted on a horizontal shaft rotating at 1725 rpm in an 8 in. length of 2 in. stainless steel pipe having flanged ends. The mixture of soybean oil and recycle wash water was heated to 98 C as it was pumped through the preheater, but after passage through the contactor and transfer lines, the temperature fell to about 85 C at the separator inlet. Water discharged from the separator, a Westphalia Model SAOH205, was slightly cloudy to cloudy in appearance. It was recycled to the cation exchanger without cooling.

The cation exchanger used in the pilot scale tests consisted of a 2 ft length of 4 in. i.d. glass pipe filled to 8 in. with Amberlite IR-120 resin (Rohm & Haas Co.). Water flow through the resin bed was by gravity.

During operation of the oil washing system, after pH equilibrium was reached, samples of water and oil to and

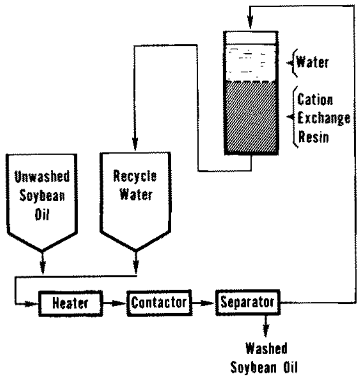

FIG. 1. Water-recycle system for washing soybean oil to remove metal cations.

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TABLE I

Removal of Sodium From Soybean Oil by Three Types of Contactors

Contactor	Water pH, to contactor	Feed ratios oil-water, v/v[a]	Sodium content, ppm		
			Water to	Oil	
				To[b]	From
Centrifugal contactor	3.4	1.7	0.04	7	1.1
Rotating disc contactor	2.9	2	0.1	10	1.1
Contactor-centrifuge	3.2	2	3.5	13	0.07

[a] Oil feed rate 100 ml/min to rotating disc contactor, 85 ml/min to a centrifugal contactor and 200 ml/min to contactor-centrifuge.

[b] To and from refer to oil and to and from contactors.

from the contactor were taken at 1/2 hr intervals for 1 1/2 hr and analyzed to make certain that operating equilibrium was attained. The initial wash water was prepared from distilled water adjusted to the desired pH with the selected acid as described later. pH of water to and from the contactor was determined at 1/2 hr intervals.

Oil and water samples were analyzed for sodium by flame photometry (4), for copper by atomic absorption and for nickel at high levels by atomic absorption and at low levels by ashing and colorimetric analysis.

RESULTS AND DISCUSSION

Tests made with a laboratory high speed blender and observations made during pilot tests showed that an important key to effectiveness of the soybean oil washing operation was the degree of mixing given the oil and water phases. For this reason a single stage, contactor-centrifuge system can wash metal cations more effectively from the oil than a multistage countercurrent system in which a high degree of mixing is not achieved in each stage of the countercurrent system.

In Table I is shown the extent to which sodium was removed during washing of an alkali-refined soybean oil in the three different contactors investigated. Because of better mixing in the single stage, contactor-centrifuge system, washed oil from this system was lower in sodium content than oil from either of the multistage systems. Equally good results would be expected if the rotating disc contactor was extended sufficiently in height.

Because the contactor-centrifuge system gave good results, was not difficult to operate, and was similar to the equipment now used in many plants for washing vegetable oils, most of the data were developed with this system.

Sodium Removal

An alkali-refined, unwashed soybean oil was processed through the contactor-centrifuge system to determine whether there was a relationship between pH of the recycle wash water and the degree of sodium removal and whether there was an optimum level of acidity in the range of 2 to 3.5 for the wash water. Within the limits of experimental error, sodium removal was essentially the same at pH's of 2.1, 2.7 and 3.2 (Table II). Distilled water at pH 7.6 gave a washed oil of higher residual sodium content and was therefore less effective than the acidic recycle water. For these tests distilled water acidified initially to the desired pH with phosphoric acid was used to start a test and then recycled through the cation exchange resin, which was in the hydrogen form. Without further addition of acid throughout a typical 6 to 8 hr test, pH of the water varied less than 0.2 units. At pH 2.1, acid strength of the wash water was 0.4% and at pH 2.7, 0.05% phosphoric acid.

In tests made with phosphate, citrate or acetate anions in the recycle washing system, all gave a high degree of sodium removal from the alkali-refined, unwashed soybean oil. For these tests, distilled water, acidified initially with phosphoric, citric or acetic acid to a pH of about 3.2, was introduced into the oil-water contactor-centrifuge system and then recycled through the cation exchange resin. Data in Table III show only small differences in sodium content of the washed oils. Recycle wash water containing the citrate or acetate anions assumed a slight orange color, an indication that minute portions of the oil may have been dispersed in the hot water discharge from the centrifuge. For this reason and because of the good sodium removal, phosphate anion is preferred in the wash water over the citrate or acetate anions.

TABLE II

Recycle Washing of Alkali-Refined Soybean Oil.
Effect of pH on Sodium Removal With PO_4Anion

Water pH		Feed ratios oil-water,[a] v/v	Sodium content, ppm		
			Water to	Oil	
To[b]	From			To	From
2.15	2.25	2	47	15	0.12
2.10	2.25	4	40	16	0.16
2.70	3.10	2	16	12	0.00
2.70	2.95	4	14	13	0.08
3.15	4.55	2	3.5	13	0.07
3.35	7.95	4	2.0	13	0.15
7.6[c]	10.35	4	0.05	22	0.57

[a] Oil feed rate, 200 ml/min.

[b] To and From refer to water or oil to contactor and from centrifuge.

[c] Distilled water.

TABLE III

Recycle Washing of Alkali-Refined
Soybean Oil. Effect of Anion Type on Sodium Removal

	Water pH			Sodium content, ppm		
			Feed ratios oil-water, v/v	Water	Oil	
Anion	To	From		to	To	From
Phosphate	3.15	4.55	2	3.5	13	0.07
	3.35	7.95	4	2.0	13	0.15
Citrate	3.20	3.65	2	4.6	7	0.12
	3.25	4.50	4	3.5	7	0.17
Acetate	3.20	4.30	2	4.1	13	0.19
	3.35	4.99	4	2.7	16	0.22
	2.75	3.25	2	11	19	0.35
	2.75	3.20	4	10	20	0.30

TABLE IV

Removal of Copper by Acidic Water-Washing
Soybean Oil Partially Hydrogenated With a Copper Catalyst

	Water pH			Copper content, ppm		
			Feed ratios oil-water, v/v	Water	Oil	
Anion	To	From		to	To	From
PO_4[a]	2.70	2.80	4	0.0	1.0	0.06
PO_4	2.85	2.95	1	0.02	1.5	0.02
PO_4	2.80	2.90	2	0.02	1.5	0.03
PO_4	2.75	2.95	2	0.02	3.6	0.22
PO_4	2.75	2.95	4	0.03	3.6	0.33
PO_4	2.05	2.15	2	0.03	19	0.53
PO_4	2.00	2.15	4	0.03	19	0.73
PO_4	3.00	3.70	2	0.03	19	1.5
PO_4	2.80	4.10	4	0.03	19	2.8
SO_4	2.75	3.00	2	0.02	3.6	0.28
SO_4	2.70	2.95	4	0.02	3.6	0.31

[a] Rotating disc contactor. All other data obtained with contactor-centrifuge.

TABLE V

Removal of Nickel From Soybean Oil Partially Hydrogenated With a Nickel Catalyst

Water pH			Nickel content, ppm[a]	
		Feed ratios	Oil	
To	From	oil-water, v/v	To	From
2.20	2.25	1	0.46	0.02
2.85	2.90	1	0.39	0.02
3.40	3.60	1	0.45	0.04
2.15	2.15	2	0.44	0.05
2.80	2.85	2	0.33	0.02
3.40	3.50	2	0.43	0.04

[a] No nickel was detected in water to contactor (from cation exchange resin).

TABLE VI

Flavor Evaluation of Recycle-Washed, Unbleached Soybean Oil

	Flavor score (peroxide value)		
Time stored at 60 C, days	Recycle-washed, unbleached oil	Water-washed, bleached oil	Significant difference
0	7.7 (0.0)	8.2 (0.0)	None
4	6.6 (0.5)	7.0 (0.5)	None
AOM (8 hr)	6.0	5.1	
Sodium, ppm	0.2	—	

TABLE VII

Estimated Fixed Capital Investment for Battery Limits Installation to Water Wash Alkali-Refined Soybean Oil by a Resin-Treated Water Recycle System[a]

Equipment installed	Cost, $
Oil feed tank, 2500 gal, S.S.	4,500
In-line blender	1,300
Heat exchanger, S.S.	3,500
Disc centrifuge, S.S.	39,000
Decanter, with receiver for supernatant oil	2,000
Two cation exchangers (acid cycle) complete with automatic controls, accessories and 6 cu ft of resin each	7,200
Surge tank, 800 gal	1,500
Four pumps, centrifugal	4,000
Engineering costs and contingencies	9,000
Estimated fixed capital investment	$72,000

[a] Plant operating schedule: 300,000 lb oil/day, 24 hr/day, 300 days/year.

TABLE VIII

Estimated Processing Costs for Water-Washing Alkali-Refined Soybean Oil by a Resin-Treated Water-Recycling System[a]

Cost item	$/day
Chemicals	
Hydrochloric acid, 100 lb 22° Bé for 2 flays, $0.02/lb	1.00
Utilities	
Electricity, 375 kwh/day, $0.015/kwh	5.63
Treated water 1000 gal/day, $0.30/M gal	0.30
Steam, 35,000 lb/day, $0.80/M lb	28.00
	33.93
Labor and supervision	
Operators, 9 man-hr/day, $4.00/hr	36.00
Supervision, 20% of operating labor	7.20
Overhead	10.80
	54.00
Maintenance, 6% on $72,000	14.40
Fixed charges	
Depreciation: 10%/year on $71,500	23.83
20%/year on $500 (resin)	0.33
Taxes and insurance, 3%/year on $72,000	7.20
	31.36
Miscellaneous factory supplies and expenses	2.16
General plant overhead	34.20
Estimated processing costs	171.05
Estimated processing costs, cents/100 lb oil	5.70

[a] Plant operating schedule: 300,000 lb oil/day, 24 hr/day, 300 days/year.

Copper Removal

Interest in partial hydrogenation of soybean oil with catalysts containing substantial amounts of copper has led to studies on ways to remove dissolved copper from soybean oil economically. Table IV gives results of tests on recycle washing of soybean oil containing various levels of copper.

When soybean oil containing 1.0 ppm copper, after partial hydrogenation with a copper-chromite catalyst, was washed in the rotating disc contactor, the copper content dropped to 0.06 ppm, a level near that of the original untreated oil (0.04 ppm). In the contactor-centrifuge system and with a copper content of 1.5 ppm initially in the oil, the recycle wash water lowered the copper content to 0.02-0.03 ppm. When oil containing 1-2% copper-chromite catalyst is exposed to air at temperatures above 50 C, appreciable amounts of copper are dissolved in the oil in proportion to the length of exposure. To examine the effect of washing a soybean oil having a high copper level, oil containing more than 19 ppm copper was prepared by mixing refined soybean oil with 2% of copper-chromite catalyst, heating to 170 C under nitrogen, cooling to 100 C and filtering. The oil was washed with recycle water adjusted to either of two pH levels. A pH level of 2.0 (PO_4 anion) left about half as much copper as at the 3.0 level.

In many pilot-plant tests, soybean oil hydrogenated with copper-chromite catalyst contained less than 1.0 ppm copper if the oil was carefully filtered and not exposed to air while warm.

Tests with soybean oil containing 3.6 ppm dissolved copper indicate that PO_4 and SO_4 anions were almost equally effective in their removal of copper.

Nickel Removal

Recycle washing of soybean oil partially hydrogenated with a nickel catalyst gave particularly effective removal of nickel (Table V). These tests were also conducted in the contactor-centrifuge system with distilled water slightly acidified initially with phosphoric acid. At pH levels between 2.2 and 3.4 nickel removal was essentially complete.

Resin Regeneration

Regeneration of cation exchange resin to convert it back to the hydrogen form after usage to remove metal cations from recycle wash water was studied to a limited extent. Capacity of the resin remaining after continued use and of freshly regenerated resin was determined by taking about 25 ml of resin in water, adding about 10 ml of saturated sodium chloride solution and titrating the resin-water with 1 N NaOH to a phenolphthalein end point. Volume of alkali solution (milliliter) per milliliter of resin is a measure of resin capacity in milliequivalents per milliliter.

Analysis of a liter of resin that had been used for recycle washing for several months in pilot-plant tests showed a residual hydrogen-exchange capacity of 0.32 meq/ml compared to about 1.6 initially. Because part of the resin appeared to be wetted with a film of oily material, a portion of the entire resin was stirred for 2 hr with near boiling 10% NaOH solution, rinsed, regenerated with 10% HCl and rinsed with distilled water until the effluent was neutral. Another portion of the original resin was regenerated without pretreatment. After regeneration, the caustic-treated resin had a hydrogen exchange capacity of 1.30 meq/ml, whereas the resin regenerated without pretreatment had a capacity of 1.56 meq/ml. This difference indicates that regeneration without pretreatment is satisfactory and that continued use of cation exchange resin in a water-recycle system should not present any problems of resin reuse for extended periods.

When recycle water at pH 2.5 was stored at room temperature and in contact with cation exchange resin for about three weeks, considerable growth of a microorganism was observed and identified as a mold. Mold mycelium accumulated at the top of the resin and obstructed water flow through the resin column. This growth should be prevented by sterilizing or discarding recycle water when the system is shut down long enough for objectionable growth to occur. During normal recycle operation (100 C) microbiological growth is not observed.

Flavor Evaluation

To determine if oil of satisfactory flavor could be prepared, an alkali-treated oil (unwashed) was washed in the centrifugal countercurrent contactor with recycle water of 3.2 pH (PO_4 anion) pumped to the contactor at a 2:1 oil-water ratio. The washed oil, which contained 0.2 ppm sodium, was deodorized directly without bleaching, and citric acid (0.01%) was added to the oil during cooling following deodorization. A quantity (1200 g) of the same refined oil was washed by mixing for 10 min at 75 C with 15% distilled water under N_2 and separating the oil by centrifugation. The centrifuged oil was bleached 15 min under nitrogen at 110 C with 1% activated bleaching clay, filtered under N_2 and deodorized as before. Flavor evaluation by a trained 15-member panel showed no significant difference in flavor scores of the two oils, either as freshly deodorized or after 4 days of storage in a 60 C oven (under air) (Table VI). The oils were unusually stable with respect to flavor and oxidation. The flavor score of a good oil after 4 days of storage at 60 C is usually about 5.7 and its peroxide value is about 2.5.

Cost Evaluation

A preliminary cost estimate for a hypothetical plant for water-washing 300,000 lb/day of alkali-refined soybean oil by a resin-treated water-recycling system shows that this process can be conducted for about 5.7 cents/100 lb of oil processed. The plant is assumed to operate 300 days per year, 24 hr per day, and requires an estimated fixed capital investment of $72,000 (Table VII). Building cost is not included as a part of the investment since this process will be operated in a soybean processing plant already established. The processing cost includes cost of the acid for regenerating the cation resin, utilities, labor and supervision, maintenance, fixed charges, miscellaneous factory supplies and expenses and general plant overhead (Table VIII). A simplified flowsheet of the process is shown in Figure 1.

The cost of water washing alkali-refined soybean oil by the usual commercial method is unknown to us. However, the recycle water-washing method should be no more costly because of the similarity in operation, because there is no loss of oil and because there is no waste-water disposal cost. Because the recycle method produced a washed oil extremely low in residual soap content (based on sodium content), some savings can be expected if the oil need not be bleached or if the amount of bleach can be reduced considerably. Cost of bleaching soybean oil, adjusted to 1970 costs, is estimated to be about 35 cents/100 lb of oil (5).

The refined oil available to the hypothetical plant is assumed to contain 20 ppm of sodium. Oil and wash water (pH 3) are heated to about 95-100 C, thoroughly mixed in a 2:1 weight ratio and centrifuged in a disc centrifuge. Oil leaving the centrifuge contains less than 0.5 ppm of sodium. Water from the centrifuge passes to a decanter to permit separation of any entrained oil caused, for example, by temporary centrifuge overload. This oil can be recovered as washed oil. Two cation exchanger columns with automatic controls are installed in the plant to remove sodium from the wash water. Each exchanger can be operated continuously for two days before regeneration of the resin is required. Capacity of the resin for exchanging hydrogen ions for metallic ions is based on manufacturer's specifications for the resin. An additional quantity of resin above that theoretically required is included in the operating capacity. Resin life is expected to be five years. Either sulfuric acid or hydrochloric acid can be used for regeneration with deionized water being used for washing the resin free of acid.

Soybean oil with a considerably higher sodium content than 20 ppm could easily be processed in this hypothetical plant without substantially adding to the processing costs. For example, if the oil contained 40 ppm sodium instead of 20 ppm, regeneration of the resin would be required daily instead of every two days. Since the cation exchangers are automatically controlled, the only additional cost involved would be for increased acid consumption for resin regeneration. Acid costs are a minor charge to the process. Labor costs would remain the same and no changes in equipment would be anticipated. Overall labor requirements for the process are low and after start-up, little attention would be required to keep the equipment in operation.

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