Water Recycle Method for Washing Alkali-Refined Soybean Oil[1]

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Abstract

Vegetable oil refineries are faced today with cutting down on pollution caused by their waste water. A method was developed for washing alkali-refined soybean oil with treated, recirculated wash water. In this method, wash water passes through a cation exchange resin that removes Na, and the slightly acid water goes back into the system for continuous reuse. The disposal problem arising from current industrial practice can be largely or entirely avoided by this reuse method. The new method might well be applicable to other oilseed processing. Batch tests were first made by mixing water, alkali-refined soybean oil and cation exchange resin. The amount of Na in the soybean oil was reduced from 34 to less than 0.5 ppm. In continuous washing tests conducted in a Podbielniak contactor with water treated by a cation exchange resin, the Na level of a commercially refined oil (not water-washed) was reduced from 34 ppm to less than 1.5 ppm. These results are comparable to or better than those obtained by the conventional method of employing fresh water for washing soybean oil.

Introduction

The common method of refining soybean oil for food use in the United States is to treat the crude oil with a caustic soda solution to convert free fatty acids (FFA) to oil-insoluble soaps and to precipitate certain oil impurities, such as phosphatides and other materials (1). Primary centrifuges separate the resulting soapstock from the oil. The oil from the primary centrifuges is washed continuously with 10–20% hot water, at approximately 170 F. The wash water-oil mixture is sent to secondary centrifuges, which separate the water and residual soap from the oil. The washed oil goes to a vacuum dryer to reduce the moisture content to about 0.1%, while the wash water containing both soap and emulsified oil is discarded to the sewer system. Sometimes the wash water is given an acid treatment to convert soaps to FFA and break the emulsion. After separation of oily constituents the water is neutralized before disposal.

This paper introduces a modification to the conventional washing procedure. In the new method wash water is put through a bed of cation exchange resin in the H form and reused continuously. Minor amounts of makeup water are added as required to replace losses. This process, if successful on a manufacturing scale, would make it unnecessary to dispose of wash water and would thus eliminate a water pollution problem. As water recycled to the washing process is slightly acidic, problems with soap and emulsified oil are eliminated. The recycle method should also be applicable to washing alkali-refined cottonseed and other vegetable oils.

TABLE I
Effect of Mixing Time on Sodium Removal From Alkali-Refined Soybean Oil in Batch Tests[a]

Mixing time, min	Product oil	
	Na, ppm	Soap, ppm (Na × 13.2)
0	34	450
3	2.5	33
5	0.1	1
10	0.3	4
15	0.3	4

[a] Oil-to-wet resin ratio, 20; oil-to-water ratio, 3.3; mixing speed, 900 rpm; temperature, 25 C.

Experimental Procedures

Soybean oils alkali-refined, but not water-washed, were obtained from Arkansas Grain Co. to get representative industrial oils. The first lot of oil contained 34 ppm Na and 0.035% FFA; a second lot, 7 ppm Na and 0.02% FFA.

Amberlite IR-120, a medium-porosity cation-exchange resin, in the H form, was used to remove Na ion from the wash water for all tests. The resin as received was washed with distilled water and filtered on a Buchner funnel under vacuum to remove excess water. The resin, which finally contained about 50% water, was used in this wet form.

Batch Tests

Batch washing tests were made in glass beakers with lot 1 refined soybean oil (not water washed), cation exchange resin, and water. They were mixed

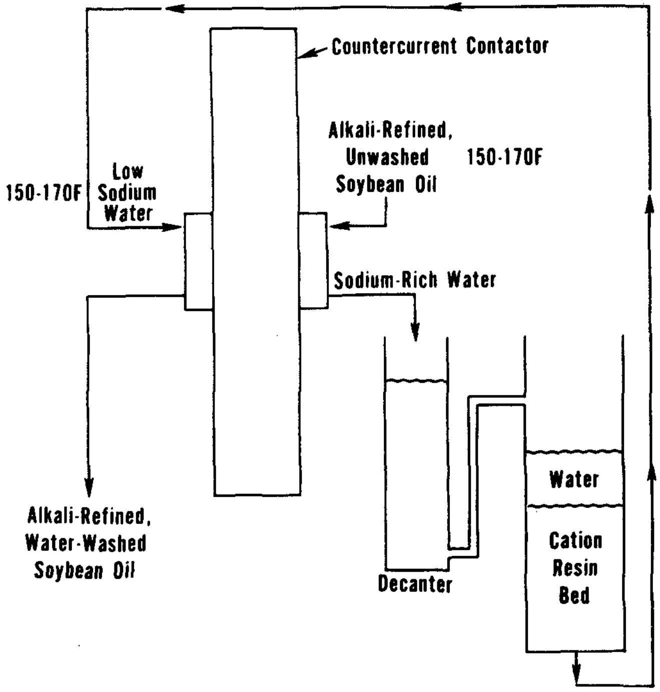

FIG. 1. Flowsheet of continuous cation exchange-water recycle method of washing alkali-refined soybean oil.

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TABLE II
Comparison of Distilled, Batch Ion-Exchange, and Continuous Ion-Exchange Water Washing of Alkali-Refined Soybean Oil[a]

Test	Length of test, hr	Soybean oil out of contactor			Water to ion exchange column			Water from ion exchange column		
		Na, ppm	Soap equivalent,[b] ppm	FFA, %	Na, ppm	Soap equivalent,[b] ppm	pH	Na, ppm	Soap equivalent,[b] ppm	pH
Distilled water	2½	2.1	28	0.05			Water out of contactor 40 ppm Na			
	3	2.0	26	0.035						
	3½	2.1	28	0.035						
	4	2.3	30	0.035						
	4½	2.1	28	0.035			↓		↓	
Batch ion-exchange water	1	1.4	18	0.04			Water out of contactor 40 ppm Na			
	1½	1.4	18	0.04						
	2	1.7	22	0.04						
	2½	1.8	24	0.04						
	3	1.3	17	0.045			↓		↓	
Continuous ion-exchange water	1½	2.0	26	0.035	32	422	10.1	6.9	91.0	5.7
	2½	1.5	20	0.045	38	502	7.6	3.5	46.2	3.7
	3½	1.3	17	0.05	38	502	7.5	5.0	66.0	3.6
	4½	1.4	18	0.05	38	502	7.4	6.9	91.0	3.4
	5	1.3	17	0.055	38	515	7.0	8.9	117.4	3.3

[a] Original oil, 34 ppm Na, 0.035% FFA.
[b] Soap equivalent calculated (13.2 × ppm Na).

vigorously on a Magna Stir plate. At the end of a specified mixing period the oil-water-resin mixture was transferred to a separatory funnel, and the oil layer was removed and filtered to remove traces of resin. The oil layer was analyzed for Na content by direct flame photometry as described by Black (2) and for FFA content.

Continuous Tests

The ion-exchange column used in continuous tests was fabricated from a 4 in. i.d. × 24 in. glass pipe. The bottom of the column was fitted with a fine stainless steel wire screen to prevent resin leakage. Four pounds of wet catin-exchange resin (50% H_2O) was placed in the column.

Continuous tests of water-washing soybean oil were carried out in a Podbielniak centrifugal contactor (pilot-plant size, Pup model). Fig. 1 is a flowsheet of the procedure used. Soybean oil (alkali refined, unwashed) and water were heated to facilitate phase separation and pumped through the contactor in a countercurrent manner to remove Na from the oil. The contactor rotor was operated at 4300 rpm. Distilled water was used to begin the cycle and small amounts of distilled water were added during the tests to replace sampling and evaporation losses. Water, containing Na ions, went from the contactor through a decanter to separate oil and prevent it from contacting the resin bed. Oil carry-over only occurred when the equipment was first placed in operation or when feed rates to the contactor exceeded its capacity to separate the phases. From the decanter the water then went through a cation resin bed (H form) to replace Na ions with H ions. Water leaving the resin bed had an excess of H ions (pH about 3.5) and when it again passed through the contactor and came in contact with the soap in the oil, H ions replaced Na ions to form FFA which were discharged with the oil stream. Samples of the wash water into and out of the ion-exchange column were analyzed for pH and Na content; samples of the oil leaving the contactor were analyzed for FFA and Na content.

Three tests were made in the Podbielniak contactor, all with lot 1 oil. In the first test the oil was washed with distilled water. Water from the distilled water test was collected and later treated with cation exchange resin (batchwise) to remove Na ions; this treated water was used in a second test. A small amount of distilled water was used to start the third test but the wash water from the contactor was continuously passed through the bed of cation-exchange resin and reused. Soybean oil was pumped into the contactor at about 150 F and the treated water was pumped in at about 170 F. Exit oil and water streams had respective temperatures of about 170 and 145 F. Oil and water input rates were 52 and 48 cc/min, respectively. The distilled water test was conducted for 4½ hr, the batch ion-exchange water test for 3 hr, and the continuous ion-exchange test for 5 hr.

Tests to determine whether recirculated wash water was effective in removing Na from soybean oil for longer periods were conducted for 8 hr on 3 consecutive days (total of 22¼ hr) (lot 2 oil). Oil and water feed rates to the contactor were kept

TABLE III
Continuous Recycle Washing of Alkali-Refined Soybean Oil[a]

Length of test, hr	Flow rates, cc/min		Washed soybean oil		Water into ion exchange column		Water out of ion exchange column	
	Oil	Water	Na, ppm	FFA, %	Na, ppm	pH	Na, ppm	pH
1¾	85	70	1.5	0.025	5.7	6.6	0.4	4.0
3¾	85	70	1.4	0.03	4.3	6.4	0.1	3.9
6¾	85	70	1.3	0.035	5.0	5.2	0.1	3.7
7¾	85	70	1.2	0.03	4.2	5.0	0.0	3.6
10¼	85	70	1.7	0.025	3.5	4.3	0.0	3.6
12¼	85	70	1.3	0.03	3.5	4.5	0.0	3.6
14¼	85	70	1.3	0.03	3.6	4.4	0.0	3.4
16¾	85	70	1.8	0.03	3.9	4.0	0.1	3.4
17¾	85	50	1.4	0.03	6.5	5.4	0.0	3.4
18¼	85	50	1.1	0.03	6.5	4.1	0.0	3.4
19¼	85	35	1.1	0.03	10.2	4.8	0.0	3.3
19¾	85	35	1.2	0.03	9.6	4.8	0.0	3.3
20¾	85	25	1.2	0.025	25.8	5.8	0.0	3.4
21¼	85	25	1.2	0.025	12.1	5 1	0.0	3.4
22¼	85	115	1.1	0.025	2.1	3.5	0.0	3.3

[a] Original oil, 7 ppm Na, 0.02% FFA.

TABLE IV
Taste Panel Evaluation of Soybean Oils

Treatment	Average flavor scores				Significance
	Conventional soybean oil, 1% bleach	Recycle washed soybean oil			
		0% Bleach	0.5% Bleach	1.0% Bleach	
Initial	7.5(0.0)[a]	5.4(0.0)	7.4(0.0)	7.7(0.0)	b
60 C, 7 days	3.2(3.7)	5.3(1.4)			b
60 C, 7 days	4.1(3.1)		5.1(3.7)		b
60 C, 7 days	4.1(3.7)			5.1(1.6)	b
60 C, 7 days		5.7(0.9)	4.3(3.5)		b
60 C, 7 days		6.2(0.9)		4.6(1.6)	b
60 C, 7 days			5.1(3.4)	5.4(1.7)	c
Average 7-day score	3.8	5.7	4.8	5.0	
AOM, 8 hr	12.3	8.4	11.8	4.6	
Lovibond red	1.1	1.2	1.0	1.1	
Lovibond yellow	10	10	10	10	

[a] Figures in parentheses are the peroxide values of the oils.
[b] Highly significant difference.
[c] No significant difference.

constant at 85 and 70 cc/min, respectively, for the first 16¾ hr of operation. After this time the oil rate was held constant and water input was varied from 25 to 115 cc/min to determine the effect of water-to-oil ratio on the amount of Na left in the oil. Input and exit oil and water contactor temperatures were about the same as in the previous tests. A total of 30 gal of oil was washed during the test. The amount of water in the system, including that held in the contactor, ion-exchange column, and feed container, was less than 3 liters and no significant loss of water occurred.

A 5 gal sample of washed oil containing 1.2 ppm Na was collected during the 22 hr test and further processed in the laboratory for flavor evaluation. Portions (1200 g) of the oil were bleached under nitrogen with various amounts of activated bleaching earth for 15 min at 110–115 C and, after cooling, were filtered under nitrogen on a Buchner funnel. To prepare a control oil for flavor evaluation, a sample of the original refined, but unwashed, soybean oil was washed by vigorously mixing it with 15% distilled water for 10 min and recovered by centrifuging for 30 min. The washed oil was vacuum-dried and bleached with 1% activated earth by the same procedure used with the other samples.

The control oil, washed and bleached by the conventional method, and samples of oil from the continuous recycle washing test which were bleached with 0.5% and 1% bleach, and a nonbleached sample, were deodorized 4 hr at 210 C, 1 mm abs. Citric acid (0.01%) was added to each sample as it was being cooled in the deodorizer. The deodorized oils were evaluated for taste by a 15-member panel at the Northern Laboratory (3).

Results and Discussion

Batch Tests

Mixing time affects how much Na ions is removed by cation-exchanged resins as shown in Table I. The mixing time was increased from 3 to 15 min in tests conducted at 25 C, 900 rpm, oil-to-wet resin ratio of 20 (2.5% resin, dry basis) and at an oil-to-water ratio of 3.3. At mixing times of 5 min or greater the sodium level in the oil was reduced to about 0.3 ppm. Removal of other metals (Ba, Cu, Cr) from soybean oil with a batch oil-water-cation-exchange resin system has been described (4).

Continuous Water Washing

Results of the continuous washing tests conducted with distilled water, with batch ion-exchange water, and with continuous ion-exchange water are shown in Table II. In the test in which distilled water was used to wash soybean oil, the amount of Na remaining in the oil was approximately 2.0 ppm; whereas in both tests with water treated with cation exchange resin, approximately 1.5 ppm Na remained in the oil. The amounts of FFA in the oil samples were slightly greater than in the original soybean oil. The water leaving the contactor contained about 40 ppm Na ion for all samples regardless of the type of wash water employed. During the 5 hr continuous test, the pH of the wash water from the contactor decreased from 10.1 to 7.0 and the pH of the water leaving the ion exchange column decreased from 5.7 to 3.3. It is typical of all continuous tests we have made that the pH of the water leaving the cation exchange-resin column falls to about 3.5 and then remains nearly constant during extended water recycle operation. The principal anion in the recycle water, after 14 hr of continuous recycle washing operation was PO_4; small amounts of Cl, SO_4 and NO_3 were also present.

The oil used in the 22¼ hr test (summarized in Table III) contained 7.0 ppm Na and 0.02% FFA. Distilled water was used to start the run, and only minor amounts of water were added to the system during the run to replace sample and evaporation losses. The pH of the recirculated water going into the ion-exchange column gradually decreased from 6.6 to 4.0 during the first 16¾ hr of operation, and the pH of the water coming from the ion-exchange column dropped from 4.0 to 3.4. Since water out of the ion-exchange column contained only trace amounts of Na ion, the cation exchange resin was efficient. The soap (calculated from Na content) remaining in the water-washed soybean oil was less than 20 ppm for most samples. This amount of soap is approximately that remaining in a conventionally processed soybean oil after water washing (Bloomberg, private communication). There was little FFA buildup in the oil, and in the range tested water input rate to the Podbielniak contactor had no effect on the amount of Na remaining in the oil.

Taste Panel Evaluation

Results of taste panel evaluation of samples from the 22¼ hr test (Table IV) show that initial flavors of the deodorized oils which had been bleached are not significantly different but that the unbleached, deodorized oil has a significantly lower flavor score. Flavor scores of 8 and 9 are considered good for oils, while scores of 6 and 7 indicate intermediate quality, and scores of 4 and 5 signify poorer oils under the scoring system used (3). Most oils, deodorized in the laboratory, receive average scores of about 7.5 to 8.0. Samples washed by the recycle method received significantly higher flavor scores than the control oil after 7 days' storage at 60 C. The unbleached sample apparently suffered no flavor deterioration during storage and was scored significantly higher than all samples that had been bleached. Better oxidative stability is also indicated by a lower peroxide value (Table IV). Samples of the recycle washed oil bleached with 0.5% and 1% activated earth were not significantly different in stored flavor scores.

The AOM 8 hr peroxide value was lowest for the recycle washed oil that received 1% bleach. Lovibond colors of the deodorized oils followed more or less the expected pattern, with the unbleached oil having the highest color.

These data indicate that soybean oil washed by the recycle method may be bleached and deodorized to give a satisfactory soybean salad oil. Indications that the recycle washed oil may even give a superior salad oil need to be further tested.

ACKNOWLEDGMENT

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