Water-Recycle Washing of Refined Soybean Oil: Plant Scale Evaluation[1]

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ABSTRACT

A series of 24 hr tests was made in a commercial refinery under eight different operating conditions to select optimum conditions for a subsequent longer test of the antipollution recycle-washing process wherein wash water is recycled instead of being discarded. Alkali-refined oil was continuously washed at a rate of 15,000 lb/hr to remove sodium. Recycled wash water was then treated with a cation exchange resin to remove sodium. Two wash water pH levels, two oil-water ratios and the addition of a sequestering agent ethylene diamine tetraacetic acid (EDTA) to wash water were factors investigated. For the longer test a water pH of 3.0 and an oil-water ratio of 4:1 were used, and EDTA was not added. Operating and analytical data, equipment specifications and cost data were acquired. The washed oil had a satisfactorily low content of sodium, iron and copper. After it was bleached the oil hydrogenated at a rate comparable to that of a conventionally washed oil. The bleached, deodorized oil had satisfactory flavor and flavor stability. The exchange resin required periodic caustic cleaning to maintain capacity. The new recycle process provides an economic solution to the wash water disposal problem.

INTRODUCTION

Disposal of wastewater from conventional washing of alkali-refined soybean oil presents a problem to refiners because of increasingly stringent laws regarding vegetable oil refinery effluents. About 0.5% of the oil washed is lost in the wastewater (R.A. Eisenhauer, unpublished data). Previous small scale tests (1-3) indicated the feasibility of a process for washing alkali-refined soybean oil to remove soap cations wherein the wash water is recycled instead of being discarded. Since the usual washing process produces a high biological oxygen demand (BOD) effluent as well as a loss of oil, the recycle process offers a two-fold benefit of increasing oil yield and reducing the wastewater effluent and BOD. In order to fully evaluate water recycle washing on a commercial scale, tests were conducted in a production refinery at a rate of six tank carrs of oil per day under a contractual arrangement. These tests provided data for an assessment of operating factors which could not be realistically evaluated in our pilot scale tests.

The test program was conducted in two phases. A series of eight 24 hr tests was made with three operating variables at two levels each. At the conclusion of preliminary tests, operating conditions were selected from the results for a 28 day semicontinuous operation in which the recycle washing process was used 5 days per week, 24 hr per day, except for shut-down periods to be described later.

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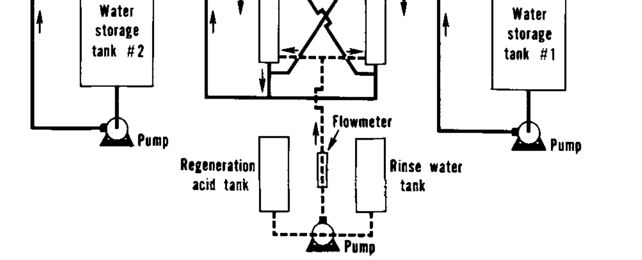

FIG. 1. Recycle washing flowsheet.

EXPERIMENTAL PROCEDURES

Analytical

Sodium in refined oil was determined by flame photometry and copper and iron by atomic absorption (4,5). BOD in wastewater was determined by the standard 5 day method (6). Free fatty acids were determined by the AOCS method (7). The 8 hr AOM peroxide value was determined by oxidizing a sample of deodorized oil 8 hr under standard conditions (8) and determining peroxides (9).

To determine the susceptibility of refined oil to hydrogenation, samples (both unbleached and laboratory bleached [0.5% Super Filtrol 15 min at 105-110 C] oils) were hydrogenated for 30 min in a Parr Autoclave modified with a gas dispersion stirrer, with 0.05% Girdler G-15 reduced nickel catalyst, at 175 C, 10 psig hydrogen pressure. Samples taken after 15 and 30 min reaction were analyzed for refractive index (40 C) and iodine value.

Operation

Equipment consisted of two 1500 gal fiberglass storage tanks, two 8 ft^3 rubber-lined ion exchange columns, two stainless steel centrifugal pumps, a flowmeter, heat exchanger, Lightnin no. 2LBS-50 in-line mixer, water wash centrifuge, 16 ft^3 of Amberlite 252 cation exchange resin (Rohm & Haas Co.) and a level control for no. 1 storage tank. The flowmeter, heat exchanger and mixer were of stainless steel. The centrifuge had stainless discs and dam but had a carbon steel bowl, dam retainer ring and cover. The retainer ring and cover underwent severe corrosion during the tests and the cover required repair, but the steel bowl was not affected by the slightly acid wash water. All pipe and fittings were of fiberglass or stainless steel construction.

A flow diagram of the system for washing alkali-refined soybean oil to remove soap cations is illustrated in Figure 1. The original oil was nondegummed crude. Steam condensate with pH adjusted to desired level with phosphoric acid was placed in water storage tank no. 2. The water was pumped through the flowmeter into the heater together with alkali-refined, unwashed oil, and then to the mixer at 180-190 F and centrifuged. During mixing, sodium ions in the oil exchange with hydrogen ions in the water. Refined,

TABLE I

Preliminary Runs, Average Data

No.	pH	Oil-water	EDTA[a], %	Sodium, ppm Unwashed oil	Sodium, ppm Washed oil	Sodium removed, %
1A	2.5	2.5:1	0.0	68	0.6	99.1
1B	2.5	5:1	0.0	47	1.8	96.2
2A	3.0	5:1	0.	40	1.9	95.3
2B	3.0	5:1	0.0	46	2.1	95.4
3A	2.5	2.5:1	0.01	48	1.4	97.0
3B	2.5	5:1	0.01	34	0.5	98.5
4A	3.0	2.5:1	0.01	50	1.3	97.4
4B	3.0	5:1	0.01	25	2.3	90.8
			Averages			
	2.5					97.7
	3.0					94.7
		2.5:1				97.2
		5:1				95.2
			No			96.5
			Yes			97.4

[a]EDTA = ethylene diamine tetraacetic acid.

washed oil from the centrifuge then was vacuum-dried before subsequent treatment. Water from the centrifuge was stored in water storage tank no. 1. From there it was pumped, at ca. 150-170 F, through two cation-exchange resin columns in series and collected in tank no. 2 for reuse. A recording pH meter monitored the water from the primary ion-exchange column and signaled by a rising pH when regeneration of the primary column resin with sulfuric acid was required. During regeneration of the resin in this column, recycle water was passed only through the secondary column. After regeneration, the fresh column became the secondary column. In this manner, the two columns were alternately regenerated for reuse as they became exhausted of hydrogen ions and saturated with sodium and other metal ions.

Resin regeneration was conducted as follows: (a) The exhausted resin (8 ft^3) was backwashed in the column with 100 gal of plant water at a rate of 10 gal/min. (b) The washed resin was backwashed with 2500 lb of 2.5% sulfuric acid at a rate of 7.5 gal/min (for 40 min). (c) The resin was backwashed with 4.75 gal/min of plant water for 40 min. (d) The resin was down-rinsed with 20 gal/min of plant water for 30 min. (e) The resin was down-rinsed with 20 gal/min of recycle water from tank no. 1 for 10-15 min.

TABLE II

Continuous Runs, Average Data[a]

Day	Flow, lb/hr Oil	Flow, lb/hr Water	pH, from tank no. 2	Sodium, ppm[b] Unwashed oil	Sodium, ppm[b] Washed oil	Free fatty acid, %
1	15,640	3950	2.9	49	2.3	0.065
2	15,830	4000	2.6	58	2.0	0.075
3	15,920	3950	2.8	56	1.8	0.072
4	16,000	4000	2.8	54	2.1	0.065
5	15,670	3950	2.8	20	2.4	0.059
6	15,600	3950	2.9	17	2.6	0.063
7	15,600	3900	3.1	8.7	2.9	0.063
8	15,600	3900	3.0	8.9	2.9	0.063
9	15,710	3900	3.1	31	3.6	0.065
10	16,000	3900	2.8	39	6.4	0.063
11	15,600	3900	2.8	26	1.2	0.060
12	15,600	3900	2.9	28	1.4	0.053
13	15,600	3900	2.9	30	1.8	0.067
14	15,200	3750	3.0	26	1.7	0.050
15	15,000	3650	3.0	32	1.9	0.050
16	14,850	3650	3.0	48	2.5	0.060
17	14,320	3650	3.1	37	2.2	0.060
18	14,890	3550	3.0	59	3.1	0.068
19	14,660	3700	2.9	35	2.5	0.057
20	10,730	2700	3.0	32	2.3	0.055
21	9530	2350	3.0	23	1.7	0.047
22	12,380	3100	3.0	34	2.3	0.057
23	13,330	3350	2.9	26	0.9	0.053
24	13,380	3350	2.9	35	0.4	0.055
25	13,170	3300	2.9	34	1.8	0.057
26	12,730	3200	2.8	61	1.1	0.080
27	13,470	3350	2.9	31	1.6	0.062
28	13,880	3450	2.9	35	1.6	0.050
Average	14,500	3600	2.9[c]	35	2.2[d]	0.061

[a]Spot analyses of samples of washed oil for iron and copper gave: Fe, 0.02-0.09 ppm; Cu. 0.02 ppm.

[b]Sodium x 13.2 = soap (theory).

[c]pH of recycle water from tank no. 1 to ion exchange column was generally 3.5-5, but occasionally 8-10.

[d]Average sodium removal, 93.7%.

TABLE III

Hydrogenation for Soybean Oil Washed by Recycle and Regular Methods

	Extent of hydrogenation[a]			
	Refractive index, 40 C		Iodine value	
Sample	15 min	30 min	15 min	30 min
Regular washed				
Unbleached	1.4627	1.4609	98.6	83.4
Bleached[b]	1.4609	1.4590	85.1	67.8
Recycle washed				
Unbleached	1.4656	1.4648	124.2	117.8
Bleached	1.4613	1.4596	88.9	72.6

[a]Initial refractive index: 1.4668. Initial iodine value: 131.8. Hydrogenation conditions: 175 C, 10 psig, 0.05% Girdler G-15 catalyst.

[b]0.5% Super Filtrol, 15 min at 105-110 C.

All rinse and regeneration effluents were discarded. During the 28 day test, it was found that the time between regenerations dropped from 20 hr to less than 2 hr after ca. 9 days of operation. It was then necessary to soak the resin in situ with hot 2% caustic solution for 2 hr to remove impurities. When the resin was then regenerated with acid, it was restored to a satisfactory capacity. When the recycle washing system was shut down for longer than 1 day, acid was added to the water in the resin columns to inhibit the growth of microorganisms.

During the course of the experiment, hourly records were made of the oil flow, wash water flow, pH to the ion-exchange column, temperature to the ion-exchange column and temperature from the mixer. The pH to the heater was monitored every 30 min, and the pH from the primary ion-exchange column was continuously monitored. Samples of the wash water to the heater and from the centrifuge and of the unwashed and washed soybean oil were collected every 8 hr for sodium and fatty acid analysis.

RESULTS AND DISCUSSION

Preliminary Runs

In preliminary runs, pH's of 2.5 and 3.0, oil-water flow ratios of 5:1 and 2.5:1 and the addition of EDTA were operation variables examined. The results of the eight 24 hr runs are outlined in Table I.

From these results, the best conditions for removing sodium were pH 2.5 and oil-water 2.5:1. EDTA had negligible effect.

Difficulty was encountered during the preliminary run 2B in the first attempt to maintain a pH of 3.0. The pH dropped well below the operational limits of 3.0 ± 0.2. Consideration of the problem indicated that significant anion contamination was introduced from the raw water originally used for the final rinse of the ion-exchange columns following regeneration. To overcome the problem two procedures were tried: (a) using steam condensate to rinse the resin (step *e*); and (b) using recycle wash water from storage tank no. 1 to rinse the resin (step *e*) and then adding condensate to tank no. 1 to replace water removed. Both procedures were found to be successful, but the latter was used because it offered a faster, more steady flow rate. It was then possible to maintain the pH within desired limits in run 2B and succeeding runs.

TABLE IV

BOD Tests[a]

Cycle	BOD_5, mg/liter	Water, lb	BOD lb
(a) Backwash	10,500	830	8.7
(b) Inject acid	2340	2420	5.8
(c) Displace acid	980	1580	1.5
(d) Fast rinse	140	5000	0.9
Total		9830	16.9

[a]Assuming the final rinse (e) is made with steam condensate and no BOD material is removed.

TABLE V

Estimated Fixed Capital Investment for Installation of Equipment to Convert a Normal 12 Tank Car Per Day Refinery System to a Recycle Water Wash System

Equipment	Cost in dollars
Heater	1000
Mixer	1500
Two tanks, fiberglass	1900
Two pumps	1400
Motor control valve	200
Two cation exchange columns, fully automated, with 30 ft^3 resin per column	24,200
Total equipment cost	$30,200
Installation (in existing facility)	5000
Estimated fixed capital investment	$35,200

Continuous Run

Operating conditions used for the continuous run were: pH of 3.0, oil-wash water flow ratio of 4:1 and no EDTA. Selection of the 3.0 pH was made on the basis of its less corrosive effect than the 2.5 pH. The flow ratio was chosen to give as low a ratio as possible and still maintain some excess design capabilities of the centrifuges and their wash water discharge piping.

Results obtained during the 28 day continuous run are summarized in Table II. Average sodium removal was 93.7%. Several samples of washed oil analyzed during the run contained 0.02-0.09 ppm Fe and 0.02 ppm Cu.

The quality of bleached oil produced by the recycle water wash system was equal to the quality of bleached oil produced using conventional washing techniques.

A sample of refined soybean oil washed by the regular method with fresh water and a sample washed by the recycle method were evaluated for their rates of hydrogenation in laboratory tests. Both samples were taken from the vacuum dryers at about the middle of the 28 day test. A portion of each sample was hydrogenated without bleaching, and another portion of each oil was bleached before it was hydrogenated. Samples hydrogenated 15 and 30 min were analyzed for refractive index and iodine value (Table III). The oil washed by the regular method and not bleached hydrogenated substantially faster than the recycle washed unbleached oil. After both oils were bleached, the difference in rate of hydrogenation was small. Soybean oil is usually bleached before commercial hydrogenation. In similar

TABLE VI

Estimates Operating Cost for Recycle Washing of Alkali-Refined Soybean Oil

Cost item	Dollars per day
Chemicals	
H_2SO_4, 66° Be', 240 lb at $0.0335 per lb	8.04
NaOH flakes[a]	3.08
Labor, 4 man-hr per day at $4.00 per hr	16.00
Maintenance, 6% on 35,200[b]	7.04
Resin usage, 20% per year on $1500[b]	1.00
Estimated processing cost	35.16
Estimated processing cost,[c] dollars per 100 lb oil	0.00488

[a]Based on 38 days of experimental data.

[b]Based on 300 days per year estimated production.

[c]Based on an estimated oil production of 720,000 lb per day.

hydrogenations made with samples taken during the preliminary 24 hr recycle washing tests, results were similar but there were smaller differences in hydrogenation rates between regular washed, unbleached and recycle washed, unbleached oil.

A sample of soybean oil that was recycle washed, bleached and deodorized (unhydrogenated) in plant equipment was evaluated by the Northern Laboratory taste panel. The bleached color of the oil was 0.4 (Lovibond red). The average odor and flavor scores of the deodorized (unstored) oil were 7.4 and 7.0, respectively, and after 4 days of storage at 60 C the scores were 6.1 and 5.3. The 8 hr AOM was 15.0. These values are similar to values usually obtained with commercial soybean oil and indicate the recycle washed oil is of acceptable quality.

During recycling of wash water, soluble material accumulates in the water. Two gallons of recycle water removed from no. 1 storage tank during the 28 day test was lyophilized in a freeze drier. The residue was a soft, brown, hygroscopic material, and the recycle water contained 2.4% of this material. Analysis gave the following values: total nitrogen (Kjeldahl) 1.54%, phosphorous 6.44%, reducing sugars after acid hydrolysis 16.0%, unsaponifiable 0.6%. Esterification of a sample with methanol and gas liquid chromatographic analysis of esters showed that the fatty acids had the composition of soybean oil. The soluble material is evidently largely phosphatides and related materials, but it includes no oil per se.

The ion-exchanger columns did not operate as long as they theoretically should before requiring regeneration. The two 8 ft^3 ion-exchange columns have a theoretical sodium removal capacity of 20.0 lb each. At an oil flow rate of 355,500 lb per day and a sodium removal level of 30 ppm from the oil, the column should last ca. 48 hr in theory and at least 24 hr in practice before requiring regeneration. From the data collected, the ion-exchange column lasted an average of only 8.9 hr. This indicates that regeneration acid may have been too weak or insufficient or that partial fouling of the resin by material in the recycle water lowered effective capacity.

Wasteload

Several 5 day BOD tests were run to determine the effectiveness in reducing the pollution load of the refinery of utilizing the recycle water wash method in processing the soybean oil. It was found that the load produced during each regeneration amounted to 16.9 lb of BOD (Table IV).

The average length of service for one column was 8.9 hr at an average flow of 14,500 lb oil per hour. Thus the BOD load using the recycle washing system amounted to 0.129 lb BOD per 1000 lb oil production.

Based on an average BOD of 10,400 mg/liter for the spent wash water and a wash water flow of 20% of the oil flow, a similar calculation for the normal refinery effluent showed that 2.08 lb BOD was produced for every 1000 lb oil production.

According to these calculations, it is possible to reduce the normal BOD load from an approximately six tank car per day refinery by 1.9 lb/1000 lb oil produced (94% reduction) by employing the recycle method of water washing.

Cost

For a plant installation in a 12 car per day (720,000 lb) refinery, the estimated fixed capital investment is $35,200, assuming that a suitable centrifuge is already available. The use of two 30 ft^3 columns in a fully automated ion-exchange system would require operational labor of ca. 4 hr per day including routine analysis of samples. With this amount of labor, the cost above the normal refinery expense is estimated to be $0.00488/100 lb of oil production (Tables V and VI). This is partially offset by a water savings in the amount of $0.00069/100 lb of oil production. This evaluation of the actual cost for a permanent installation of the water wash system is based on the plant test results described.

This procedure eliminates loss of oil during washing of the refined soybean oil, while the conventional washing produces an oil loss of ca. 0.5% equivalent to a cost of $0.05/100 lb of oil processed. Thus the recycle washing process can effect both a substantial reduction in BOD discharge and an appreciable savings in the cost of plant operation.

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