Solvent Extraction of Oil From Soybean Flour II—Pilot Plant and Two-Solvent Extractions

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The process of grinding soybeans to a fine flour and extracting the flour with hexane was studied on a pilot plant scale. The crude oil from the pilot plant study had 15 ppm phosphorus and was suitable for physical refining after a light acid pretreatment and bleaching. The refined oil showed a Lovibond color of 1.4 yellow and 0.3 red. The pilot plant study also showed that grinding of the soybeans and the separation of solid from miscella were the most difficult steps in solvent extraction with fine flour.

A laboratory study on separation of miscella from meal by aqueous ethanol reduced the hold-up volume, but it did not remove all the miscella. A test with beta-carotene showed that only the miscella outside the flour particles was displaced.

Aqueous ethanol solutions used as a second solvent extracted additional nontriglyceride materials (primarily phospholipids) from the meal. Also, the free fatty acid content of the oil was increased with aqueous ethanol solution wash. The quality of the extracted crude oil was lowered by using a second solvent, but it had the advantage of needing only one centrifugation to separate miscella from meal.

KEY WORDS: Improved crude oil quality, pilot plant extraction of soy flour, phospholipids in crude soy oil, use of a second solvent to displace hexane.

Full fat soybean flour is not commonly used in the commercial solvent extraction of soybean oil, although there are reports on methods to extract oil from soybean flour (1,2). In a previous paper on the laboratory extraction of oil from fine flour, the results showed that the oil dissolved immediately, but it took five stages to separate the oil from the meal in batchwise countercurrent extraction (3). The quality of extracted oil was excellent. The crude oil contained 37 ppm phosphorus and 0.08% free fatty acids and was very light in color. A pilot plant extraction was needed to see if fine flour extraction on a larger scale yielded the same superior quality of crude oil. It was also desirable to see what kind of problems existed in handling the fine flour on a larger scale.

Due to the large hold-up volume of the fine flour, a batch countercurrent extraction required several stages to complete and to obtain a concentrated final miscella. A second solvent was tested to reduce the number of stages, to improve the separation of miscella from defatted flour and to reduce the hold-up of hexane miscella.

As a second solvent, aqueous ethanol solutions were added to the miscella/meal mixture to displace the hexane miscella that was held up by the defatted meal. After centrifuging, the upper layer was the hexane miscella, and the bottom layer contained the ethanol solution and the defatted meal (Fig. 1).

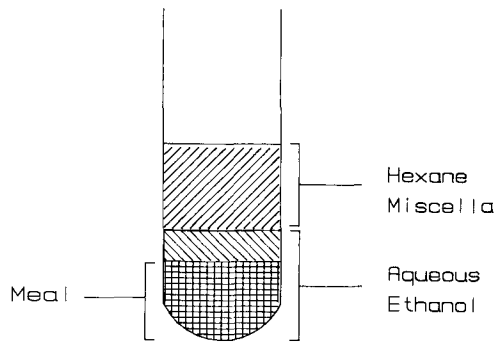

FIG. 1. Example of displacement of hexane miscella with aqueous ethanol as the second solvent. Diagram shows the result after centrifugation.

MATERIALS AND METHODS

Pilot plant study. Soybeans for the pilot plant extraction were the Centennial cultivar. The hexane used was commercial grade commonly used in solvent extraction plants.

Soybean preparation. The beans (100 kg) were cracked and dehulled prior to grinding. The cracked beans were ground in a pin mill (Alpine Contraplex Wide Chamber Mill, Type A250 Alpine American Corp., Natick, MA) without further sifting after grinding. A particle size profile was done on the resulting flour.

Oil extraction. The method used was described by Karnofsky (4) for checking the performance of continuous countercurrent extraction. The first batch was to prepare the miscellas for the second batch extraction. Only fresh hexane was used to extract the sample. Figure 2 shows the steps for the first batch extraction. The

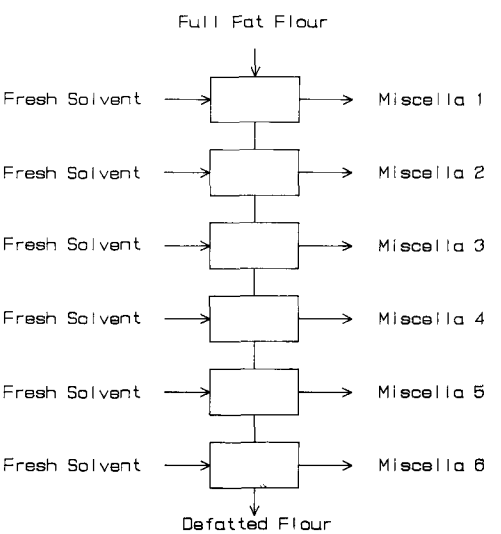

FIG. 2. Flowsheet for the preparation of the miscellas to be used in the countercurrent batch extraction.

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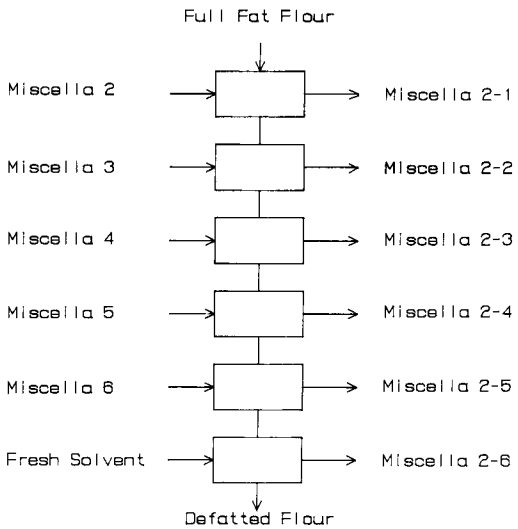

FIG. 3. Flowsheet for the countercurrent batch extraction with prepared miscellas.

solvent-to-solid ratio was 2:1 (w/w). The miscellas were collected separately, and only miscellas 2-6 were used for the second batch extraction (Fig. 3).

For the second batch, fresh flour was extracted first with miscella 2 then washed with miscellas 3-6. The sixth wash was done with fresh solvent, and solvent-to-solid ratios were 2:1 (w/w).

Flour and solvent were weighed and mixed in a mixing tank with continuous stirring. The mixture was then pumped into a Decanter centrifuge (Bird 6″ Continuous Bowl Centrifuge, Bird Machine Co., Saskatoon, SK, Canada) to separate the solids and the miscella. Centrifuging required about 15-25 min depending on the batch size and pumping rate. The pumping rate was adjusted so that the solid was wet enough to flow out of the centrifuge but would carry a minimum of miscella with it.

The residual oil content of the meal and concentration of miscella out of each stage were measured. The full miscella was allowed to settle overnight to remove residual flour and was filtered before desolventizing.

Physical refining. Crude oil was treated with 50% citric acid (500 ppm of the oil) at 45°C and bleached with 1.25% bleaching earth (Filtrol "Grade 160" Clay, Filtrol Corp., Los Angeles, CA) before being physically refined. The bleached oil was deaereated and heated first at 100°C under vacuum. Steam was then sparged at a rate of 3% w/w per hour to heat the oil at 240-250°C for one hour.

Quality evaluation of the resulting oil. Crude oil, bleached oil and refined oil were evaluated by these analytical methods: Free fatty acids, AOCS Ca 5a-40 (5); peroxide value, AOCS Cd 8-53 (6); P, Ca, Mg, Fe, Cu, ICP (inductively coupled plasma) emission spectroscopy; color, Auto-Lovibond; and chlorophyll, Auto-Lovibond.

Extraction with second solvent. The flour was prepared from whole soybeans from the Forrest cultivar, ground in a UDY Cyclone Sample Mill (UDY Corp., Fort Collins, CO) without a screen, and sifted through a 100-mesh sieve in the Alpine Air-jet Sieve (Alpine American Corp.). The particle size of the flour sample was smaller than 150 μm in diameter. The hexane used in all the laboratory extraction experiments was high performance liquid chromatography (HPLC) grade. Analytical grade ethanol (95% v/v) was used for the ethanol solutions. Displacement of hexane miscella by aqueous ethanol was done by mixing full fat flour with hexane (2:5, w/v) for one min, adding aqueous ethanol (same volume as hexane), and mixing for another 30 seconds. The mixture was centrifuged for 3 min (2500-3000 g). The upper layer was collected and the hexane was evaporated to get the oil sample. Different concentrations of aqueous ethanol solutions were tested to evaluate the ability to recover the hexane miscella. The oil content obtained from rapid equilibrium extraction with hexane described by Snyder *et al.* (7) was used as the total oil.

A dye, beta-carotene (Sigma Chemical Co., St. Louis, MO), which does not dissolve in ethanol, was used as an indicator to find out where the residual hexane miscella was after aqueous ethanol wash. The dye was first dissolved in the hexane used to extract the oil. After the hexane extraction (with dye) and aqueous ethanol wash, the orange-red color of beta-carotene will show the location of hexane miscella.

Quality evaluation of extracted crude oil. The extracted crude oil sample was analyzed for phospholipid content using the Bartlett (8) method of generating phosphomolybdate for phosphorus analysis. Absorbance was measured at 750 nm on a double-beam spectrophotometer. The triglyceride contents were calculated by subtracting the phospholipid content from total oil extracted. Five hundred grams of flour were extracted to obtain crude oil for free fatty acid analysis. Two different concentrations of ethanol were used as the second solvent. The free fatty acid analysis followed was the official AOCS method Ca 5a-40 (5). An extraction with hexane only was done on a 500-g batch. The oil sample obtained was compared with that from the second solvent extraction.

RESULTS AND DISCUSSION

Pilot plant study. The particle size profile of the flour from pilot plant pin milling is shown in Figure 4. About 97% of the flour particles were smaller than 150 μm, which was the maximum particle size recommended by Clark and Snyder (9). The pin mill reduced the particle size effectively, and no further sifting and grinding were needed.

The results for the miscella oil concentration, residual

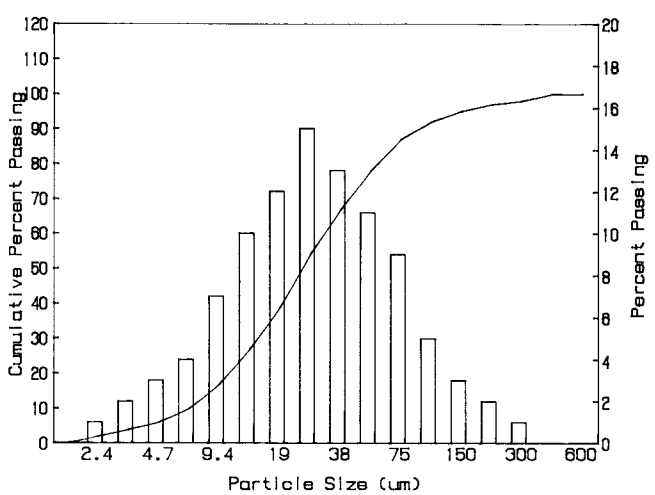

FIG. 4. The particle size profile of the flour obtained from the pilot plant pin mill.

oil content, and the percent hold-up of each stage from the second batch extraction are shown in Table 1. The percent hold-up of solvent (wet basis) was around 25% for each stage. The residual oil in the meal and miscella oil concentrations changed tremendously from step one to step two. This was caused by increased solvent-to-solid ratio. The solvent-to-solid ratio was 2:1 for the first contact of dry flour, but in the following stages, solvent was added to the wet meal. Though solvent was added at a 2:1 ratio, the actual solvent-to-solid ratio was greater than 2:1.

TABLE 1

The Oil Concentrations of Miscellas, the Residual Oil Contents (Dry Bases), and the Percent Hold-Up of the Meals from the Pilot Plant Extraction

	Miscella	Meal	
Stage	Oil conc. %	Oil content %	Percent hold-up
1	10.18	8.15	25.48
2	2.90	2.24	26.98
3	0.78	1.23	23.12
4	0.24	0.57	24.98
5	0.15	0.22	20.22
6	0.06	0.15	25.38

The quality of the extracted crude oil is shown in Table 2. The phosphorus content of the crude oil was only 15 ppm, which made it possible for physical refining after acid pretreatment and bleaching. The acid pretreatment and the bleaching steps further reduced the phosphorus to 3.7 ppm, which was below the upper limit (5 ppm) required for steam deodorization (10). The free fatty acid content at 0.18% was a little higher than the previous laboratory extraction results, which were around 0.08% (3). The Lovibond color was also higher than the previous result of 35 yellow and 1.6 red (3). The darker color from the pilot plant extraction may be caused by browning of residual flour particles during desolventization. The filtration step before desolventizing did not remove all the residual flour particles.

The pilot plant experiment showed there were difficulties in separation of the fine flour from the miscella. The fine flour did not settle easily by gravity, especially when the miscella concentration was high, and the Decantor centrifuge used in this study could not separate the flour from miscella effectively. About 90% of the solids were removed with one pass. The miscella was cloudy due to the residual fine flour, and a second centrifugation or filtration is needed to separate flour from miscella.

Extraction with second solvent. Ethanol solutions of different concentrations were used as a second solvent to reduce the hold-up volume of miscella in the fine flour. The results are shown in Table 3.

TABLE 3

The Concentrations of Total Oil, Triglyceride (TG), Phosphorus (P) and Phospholipids (PL) Recovered at Different Ethanol-Water Concentrations

Ethanol (%)	Total oil (%)	TG (%)[a]	P (ppm)	PL (%)[b]
Hexane[c]	21.49	21.48	9	0.03
90	21.00	20.45	820	2.60
85	20.36	20.12	370	1.17
65	21.02	19.89	1700	5.39
50	21.15	19.98	1740	5.52

[a] Total oil (%) and TG (%) were based on the total weight of the flour.

[b] P (ppm) and PL (%) were based on the weight of the extracted oil.

[c] Data were from the rapid equilibrium method.

From the results, it seemed that the 50% ethanol solution gave the best recovery of total oil when compared to hexane extraction. When the amounts of triglyceride (extracted oil corrected for phospholipid content) were compared, it revealed that 90% aqueous ethanol solution gave a better result than 50% solution. With 50% ethanol, a large amount of phospholipid was extracted and, therefore, that extraction resulted in the largest total amount of oil. However, none of the ethanol solutions showed 100% recovery of the triglyceride compared to the hexane extraction. Since the flour was extracted first with hexane, the oil should be dissolved before the addition of the second solvent. Therefore, there must be some hexane miscella lost in the mixture.

The result of hexane extraction with beta-carotene and

TABLE 2

The Quality and Mineral Content of the Pilot Plant Extracted Crude Oil

	Crude oil	Acid pretreated bleached oil	Deodorized oil
PV[a] meq/kg	1.95		0.01
FFA[b] %	0.18		0.0
Color	70Y 2.7R[c]		1.4 Y 0.3R[d]
Chlorophyll (ppm)	A:0.19 B:0		A:0 B:0
P (ppm)	15.1	3.7	
Ca (ppm)	1.7	0.2	
Mg (ppm)	1.2	0.2	
Fe (ppm)	0.8	0.2	
Cu (ppm)	0.1	0.1	

[a] The peroxide value.

[b] The free fatty acid.

[c] 1″ Cell.

[d] 5.25″ Cell.

the second solvent washing showed that there was a light, reddish yellow color in the defatted meal. This indicated that the hexane miscella was trapped in the flour particles and could not be displaced by the second solvent.

A test with different miscella concentrations also gave an indirect answer as to the location of residual hexane miscella. Two grams of flour were mixed with 3, 5, 7 or 9 mL hexane. The the second solvent was added to displace the hold-up volume. The amounts of oil recovered are shown in Table 4. The concentration of miscella affected the amount of oil recovered from the mixture. With higher miscella concentration (a lower hexane to flour ratio), the recovery of oil from the mixture was lower. If the flour particles trapped the same volume of miscella after the second solvent wash, the higher the concentration of the miscella, the more oil would be trapped, and the less oil would be recovered. The results supported the hypothesis that hexane miscella remained trapped in particles and was not displaced by the second solvent.

TABLE 4

Amount of Oil Extracted with Different Hexane to Flour Ratios (v/w)

Hexane/flour	3:2	5:2	7:2	9:2
% Oil[a]	18.73	20.75	21.51	21.87

[a] Based on the total weight of flour.

Using aqueous ethanol solutions as a second solvent extracted additional phospholipids and free fatty acids as compared to hexane extraction without the second solvent. Also, the quality of the crude oil was lowered (Table 5). Another shortcoming was that the second solvent did not displace all of the hexane miscella from fine flour.

TABLE 5

Free Fatty Acid (FFA), Phosphorus (P) and Phospholipid (PL) Content of Extracted Oil Samples

Ethanol (%)	P (ppm)	PL (%)	FFA (%)
Hexane[a]	39	0.12	0.14
66.6%	1585	5.02	0.64
33.3%	982	3.11	1.09

[a]Data were from the rapid equilibrium method.

Although the aqueous ethanol solution did not successfully displace the hexane miscella, it still may be useful to remove the phospholipids and some other materials soluble in polar solution to improve the quality of the defatted meal. Since Sessa and Rackis (11) have shown that oxidized phospholipids contribute to off-flavor of soybean meal, the removal of these materials should produce a more desirable food product. In addition to removal of phospholipids, the aqueous ethanol solution should remove a large portion of oligosaccharides from the meal and improve the meal for food or feed. Soy protein concentrate commercially can be made by washing the defatted, desolventized soybean flakes with aqueous alcohol. Hayes and Simms (12) reported the use of hexane and alcohol mixtures to remove the residual lipids from defatted soy flakes followed by an aqueous alcohol extraction to remove the water-soluble materials to make soy concentrate.

With fine full fat flour, after several stages of countercurrent extraction with hexane, addition of aqueous ethanol to the meal would displace the hexane and would extract phospholipids and oligosaccharides from the defatted meal. Not only could a good quality crude oil with very low phospholipid content be obtained, but concentrated phospholipids with little triglyceride content could be recovered, and an improved defatted meal would result from oligosaccharide removal in one additional step.

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