

Solvent Extraction of Oil From Soybean Flour I—Extraction Rate, a Countercurrent Extraction System, and Oil Quality

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Measurements of rates of oil extraction from either fine flour or soybean flakes in a column showed that oil extraction from flour was dependent on the volume of solvent, but oil extraction from flakes depended on time of contact rather than volume of solvent. We interpreted the data to mean that oil was being washed out of the fine flour with little diffusion involved, whereas in flakes, the limit on rate was diffusion of the solvent into and out of the tissue.

Fine full fat flour worked well in a batchwise countercurrent extraction system with mixing and centrifugal separation. Because the oil dissolved immediately and reached equilibrium rapidly, the actual material balance was close to calculated values. However, due to the large hold-up volume, the separation of miscella from the meal required several mixing and separation stages. The oil resulting from this countercurrent extraction system had a superior quality with 37 ppm phosphorus, 0.08% free fatty acids, and a light color.

KEY WORDS: Decreased phospholipids in crude oil, improved crude oil quality, rapid extraction from fine flour, soy oil extraction.

Making thin flakes is a common procedure in commercial solvent extraction of soybean oil. The traditional and accepted method of soybean preparation before solvent extraction requires many steps — receiving and cleaning, drying, bean cracking, dehulling, bean conditioning and flaking. The purpose of all those preparatory steps is to obtain a flake for high extraction rates, high drainage rates, and easy desolventizing after extraction. Grinding into fine flour, however, is not a common preparation procedure in commercial solvent extraction of soybean oil. The conventional solvent extraction equipment is designed for use with flakes and cannot handle fine particles. Grinding to a flour is used most commonly in the laboratory for analytical purposes.

It is well recognized that the rate of solvent extraction is controlled by the solid particle size (1). The reduction of particle size increases the surface area, decreases solvent penetration path lengths, and results in significantly increased oil transfer rates into the miscella.

Sheu (2) started the investigation of a new rapid equilibrium method for measuring total oil content in soybean seed using fine soybean flour. Further development (3) indicated that the particle size has an effect not only on the extraction rate, but it also increases the amount of oil extracted. Maximum oil extraction is almost instantaneous from flour that has particles smaller than 150 μm . Recent studies indicated that 98% of the extraction is completed in one min (4). The increment in amount of oil extracted is thought to be due to the increase in amount of cell tissues that were disrupted

since the intact soybean tissue is difficult to penetrate by hexane (5).

Clark and Snyder (4) reported that oil extracted from fine particles of flour by the analytical methods contains less phospholipids than the oil commercially extracted from flakes. However, grinding into flour does not guarantee a low phospholipid content. They also found that a high extraction temperature and a high moisture level of flour result in a high phospholipid content for oil from flour. For beans preheated at 130°C, even when ground into flour for extraction, the resulting oil has higher phospholipid content than the oil prepared without heating. The preheating of cracked beans and adjusting the moisture to a level of 10–11% are necessary steps for getting proper pliability of soybean to be flaked, but not for beans to be ground into flour. These preparation steps and the high extraction temperature in commercial extraction may increase the extractability of phospholipids in flakes and result in a crude oil of high phospholipid content.

It is well known that the presence of phospholipids is undesirable for processing crude oil to the final food grade vegetable oil, therefore, it is advantageous to reduce the level of these compounds as much as possible during the oil extraction process. The extraction of oil from finely ground soybean flour under controlled conditions may be a better way to obtain high quality crude oil by leaving most of the phospholipids in the meal.

Since soybeans are commercially extracted in the form of flakes, most studies on oil extraction rates have been conducted with flakes instead of flour. Particle size usually has been defined in terms of flake thickness (6,7). No study has been reported that compared the extraction rates of oil from flour and flake samples. The preparation methods of these two materials are different and so is the degree of cell destruction. Grinding the beans to a fine flour caused cellular content to be fractured to a greater extent than flaking (8).

The objectives of this study were to determine the extraction patterns of flakes and flour, the feasibility of solvent extraction from fine flour with a countercurrent system and the quality of resulting crude oil from such a system.

MATERIALS AND METHODS

Soybean flakes were obtained from a commercial source. The thickness of the flakes was about 0.25 mm. The flour was prepared from whole soybeans (if not specified it was from "Forrest" cultivar), ground in the 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., Natick, MA). The particle size of flour samples was smaller than 150 μm in diameter based on collection through the 100-mesh screen. The hexane used for oil extraction experiments was high performance liquid chromatography (HPLC) grade.

Column extraction of oil. Soybean flakes or flour were

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extracted in a glass liquid chromatography column (2.5 cm ID). The sample (about 0.5 g) was packed dry into the column to provide a layer 1 mm thick.

Oil extraction was accomplished by pumping fresh solvent (hexane) at several rates. Miscella eluting from the column was fractionally collected in aluminum weighing pans at specific time intervals. After the solvent was evaporated, the weights of oil collected at different times were recorded. Timing was started when the first drop of miscella came from the column.

Rapid equilibrium extraction. The rapid equilibrium extraction developed by Snyder *et al.* (3) was used to compare the oil extraction from flakes and flour. The sample was weighed (0.15–0.3 g) and mixed with hexane (25 mL) in a flask. After varying time, the miscella (10 mL) was pulled through a filter (Millex-PF membrane filter, 0.8 μm , Millipore Corp., Bedford, MA) using a syringe. The concentrations of the miscellas were measured by evaporating 10 mL miscella in aluminum weighing pans, and extraction curves were plotted using amounts of oil extracted vs mixing times.

The batchwise countercurrent extraction. A batchwise countercurrent extraction was conducted with mixing and separation by centrifuging (dispersed-solid leaching) to study the performance of fine flour in the countercurrent extraction system. Before starting the extraction, the quantitative performance of this extraction system was analyzed by using a graphical method with an equilibrium line and an operating line (McCabe-Thiele Plot) based on material balance at each stage to determine the number of ideal stages (9).

With the information on material balance, the operating line and equilibrium line of the McCabe-Thiele plot could easily be plotted, and the number of ideal stages was determined. How close the actual extraction was to the quantitative analysis indicated the efficiency of this extraction.

Establishment of the material balance. The information required to establish the material balance included the oil content of the starting flour, the concentration of final miscella, the residual oil content of the defatted meal, the amount of solvent used and the hold-up volume.

The concentration of final miscella was chosen so that a fairly concentrated miscella could be obtained after a reasonable number of stages. The residual oil content of defatted meal was set at 1% which is the common goal for commercial extraction. The amount of solvent required was calculated based on the total material balance that was determined by the concentration of final miscella, the amount of residual oil and the oil content of the flour. However, the oil content of the starting material and the hold-up volume had to be determined by experiment.

The oil content of the flour was determined by using the rapid equilibrium method developed by Snyder *et al.* (3). The hold-up volumes, i.e., the amount of miscella held by the solid after centrifugation (2500–3000 g) at different miscella concentrations were determined by mixing different amounts of hexane or miscella with flour. After centrifugal separation, the weights of miscellas and oils recovered were used to calculate the miscella hold-up volume.

A McCabe-Thiele plot was made from the data, and the number of ideal stages was determined. The miscella concentrations in and out of each stage were also calculated. Miscellas at the prepared concentrations were

made with crude oil and hexane. These miscellas were used in the following extraction.

The oil extraction. Full fat flour was mixed with half miscella, which is the most concentrated miscella next to the full miscella, for 2 min and then centrifuged for 3 min to separate the solid from the full miscella. The solid-to-solvent ratio used was 1:1.4, based on the calculation from the material balance. The defatted meal was then contacted with less concentrated miscellas with mixing and centrifuging at each stage.

The concentrations of miscellas out of each stage and the residual oil content of the final meal were measured and compared with calculated values from the material balance.

Quality evaluation of the extracted crude oil. An extraction of 500 g fine soybean flour was done based on the calculation of the first extraction. The crude oil used for making up the miscellas was from a laboratory extraction of the same kind of soybean flour. After the extraction, the miscellas from all the stages were pooled, filtered (Millipore FA filter, pore size, 1.0 μm) and desolventized. The miscella was desolventized in a round-bottom distilling flask heated by a heating mantle. A water aspirator was used for vacuum to help the distillation. The distilling temperature was about 70°C, and the final stripping temperature was around 150°C for 1–2 min. The final crude oil contained about 98% oil. The Lovibond color, free fatty acid and phospholipid content of the final oil were measured and compared with commercial crude oil.

A known amount of extracted oil was wet-ashed, and phosphorus was determined using the Bartlett (10) method of generating phosphomolybdate for phosphorus analysis. Absorbance was measured at 750 nm on a double-beam spectrophotometer. The free fatty acid analysis followed the official AOCS method Ca 5a-40 (11).

RESULTS AND DISCUSSION

Column extraction of oil. The column extraction of 100-mesh soybean flour was done at three different solvent flow rates. The results are shown in Figure 1a. As flow rate increased the amount of oil extracted per unit time increased. In other words, the extraction was dependent on the volume of solvent. The oil seemed to dissolve immediately after contacting the solvent and was washed out by the solvent. Flake samples showed a different pattern (Fig. 1b). No matter what the flow rate, the same amount of oil was extracted in the same time period. The oil extraction from flakes was mainly controlled by time. It seemed that diffusion was the main mechanism of the extraction.

Rapid equilibrium extraction. Mixing hexane and samples in a flask simulates the action of column extraction at maximum flow rate, except that the extraction after first contact is done by miscella instead of by fresh solvent. The results (Fig. 2) showed that extraction of flour samples was much faster than for flake samples, which were controlled by diffusion. Immediately after contact with solvent, about 95% of the total oil in the flour was dissolved. Only 10–15 seconds were needed to reach the equilibrium. If slowly dissolved oil was the cause of the decrease in extraction rate for flake samples, one would expect to see a similar phenomenon in flour samples. These results contradict the “undissolved oil” concept of Coats and Karnofsky (6). Diffusion of solvent and mis-

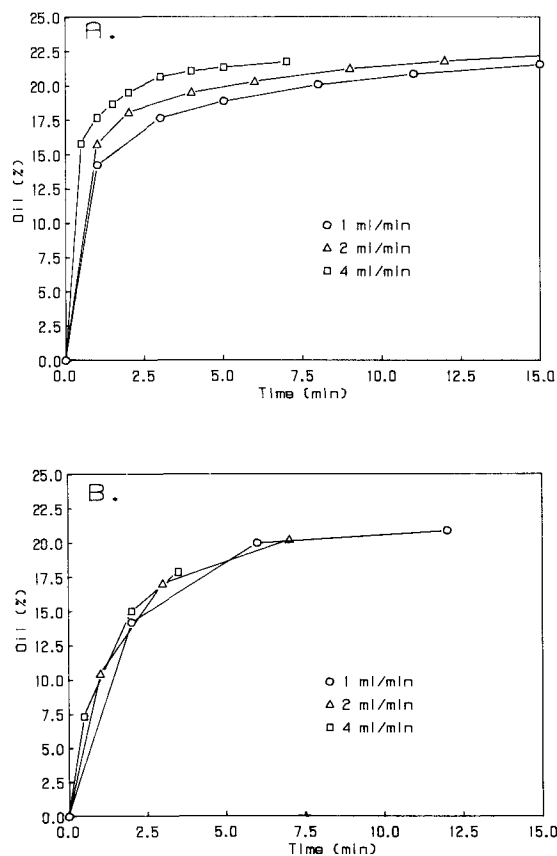


FIG. 1. Oil extraction in a column at different solvent flow rates. A, flour samples; B, flake sample.

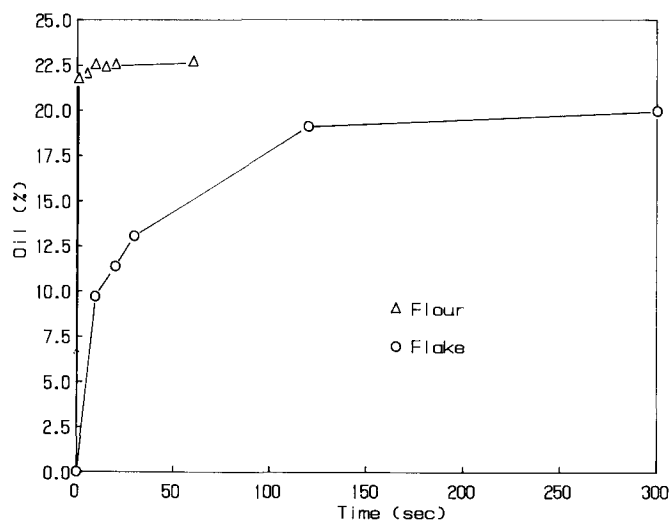


FIG. 2. Oil extraction of flour and flake samples by rapid equilibrium method (plotted by the amount of oil and extraction time).

cella in and out of the flaked tissue is still the best explanation for the slow extraction rate in flakes.

Experiments with fine, full-fat flours of soybeans showed that oil was readily extracted from flour with hexane and that it was possible to extract at room temperature instead of at elevated temperatures. If methods can be devised to handle the fine flour on a commercial scale, the rapid and complete extraction of

oil from fine soybean flour may lead to large-scale commercial extractors that would be more efficient than present equipment.

The batchwise countercurrent extraction. Due to the tendency of solvent to channel and flour to pack, the column extraction seemed incapable of handling the fine flour. Dispersed-solid leaching was suggested to handle this kind of material that formed impermeable beds either before or during leaching. The solids can be treated by dispersing them in solvent by mechanical agitation in a tank or in a flow mixer. The leached residue is then separated from the solution by settling or filtration (9).

A batchwise countercurrent extraction was conducted with mixing and centrifuging separation. The basic data for the material balance and for plotting the McCabe-Thiele plot were for the operating line: i) Concentration of final miscella, 25% (w/w); ii) residual oil of the defatted meal, 1%; iii) oil content of the full fat flour, 22.35%; and iv) hold-up volume (constant underflow), 100% of the defatted meal (w/w). Those for the equilibrium line were equal concentrations of miscella inside and outside the flour particles.

From the plot, five was the number of ideal stages determined. The calculated concentrations of miscellas and the solid-to-solvent ratio are shown in Table 1.

TABLE 1

Calculated Concentrations of Miscellas In and Out of Each Stage^a

| Stage | Concentration of miscella % (w/w) | |
|-------|-----------------------------------|-------|
| | In | Out |
| 1 | 13.16 | 25.00 |
| 2 | 6.70 | 13.16 |
| 3 | 3.10 | 6.70 |
| 4 | 1.13 | 3.10 |
| 5 | 0.04 | 1.13 |

^a Solid to solvent ratio = 1:1.4.

The results from the stage-to-stage countercurrent extraction were close to what was predicted by the McCabe-Thiele plot. The concentrations of miscellas in and out of each stage in the actual extraction are shown in Table 2.

In leaching, equilibrium is attained when the solute is completely dissolved and the concentration of the solution so formed is uniform (9). Due to the ready extraction of oil from fine flours, such a condition was obtained more easily with fine flour than with flakes. Since the oil was dissolved immediately, the stage efficiency was high and

TABLE 2

The Actual Concentrations of Miscellas In and Out of Each Stage in a Batch Countercurrent Extraction with 100-Mesh, Full-Fat Flour

| Stage | Concentration of miscella % (w/w) | |
|-------|-----------------------------------|-------|
| | In | Out |
| 1 | 13.55 | 25.00 |
| 2 | 6.67 | 13.56 |
| 3 | 3.10 | 7.03 |
| 4 | 1.15 | 3.30 |
| 5 | 0.07 | 1.24 |

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the actual number of stages was close to the number of ideal stages. The actual concentrations of miscellas in and out of each stage in Table 2 were close to the calculated concentrations in Table 1.

The most important method of leaching is the continuous countercurrent method using stages. Even in the batchwise countercurrent extraction system, the solids are not moved physically from stage-to-stage. The solids in any one stage are treated by a succession of liquids of constantly decreasing concentration as if the solids were being moved from stage-to-stage in a countercurrent system (9).

For the countercurrent extraction system with stages, it is well known that an increase in the number of stages will either increase the concentration of final miscella or reduce the residual oil content in the meal. Most of the time it can do both.

There is a question about how high the concentration of final miscella can go. Is there a limit? Since a highly concentrated final miscella is preferred, as high as possible is preferable. To answer this question it was necessary to study the material balance of the leaching system.

The concentration of final miscella was determined by the amount of solvent entering the system, the oil content of the starting materials and the residual oil content in the meal. For a leaching system using dry flour as starting material, there was a hold-up volume that had to be taken care of at the first stage. The amount of solvent used must be enough to overcome the hold-up volume to get final miscella out of the first stage. This volume puts the upper limit on concentration of final miscella.

The second factor limiting the concentration was the oil content of the flour. The higher the oil content, the higher the concentration of final miscella could be. For a flour containing 21% oil and extracted at 1:1 defatted solid/solvent ratio, the concentration of final miscella could go up to 96% (w/w), and it took more than 80 stages to complete the extraction with 1.0% residual oil in the meal. This was calculated at constant underflow basis. It would be more complicated in actual extraction, since the hold-up volume may vary due to the change of density of miscella and there may be carry-over of solids due to bad separation.

The third limit on the concentration of final miscella was the residual oil content of the meal. The lower the residual oil, the higher the potential for the concentration of final miscella. The residual oil usually is set at 1%. Reports have indicated that when the residual oil is too low, the refining loss becomes a problem because of the increased phospholipids and pigment extracted (12).

Due to the large hold-up volume by the flour (approximately 1:1 by weight), the number of stages needed to complete a reasonable extraction was a drawback. It would be desirable if the hold-up volume could be reduced.

The quality of the crude oil extracted from the countercurrent system is shown in Table 3. It was obvious that the laboratory-extracted oil was much better than the average commercial crude oil. The crude oil from laboratory extraction of fine flour was light colored and contained

TABLE 3

Quality of Crude Oil from the Laboratory Countercurrent Extraction from Soybean Flour and Comparison with the Average Commercial Crude Oil

| | Sample oil | Commercial crude |
|-------------------|------------|---------------------|
| Phosphorous (ppm) | 37 | 500-1000 |
| FFA (%) | 0.08 | 0.3-0.7 |
| Lovibond color | 34Y 1.6R | 20Y 2R ^a |

^a The value given is the trading specification for fully refined soybean salad oil by USDA.

little phosphorous and free fatty acids. The phosphorous content of the crude oil was even less than the allowable phosphorous content for commercial crude degummed oil, which has a trading specification of 200 ppm.

This result suggested that there is a way of extracting oil from soybeans that gives a much lower phospholipid content (about 1/10 or less) compared to commercially extracted crude oil. It would be possible with this high quality crude oil to go through adequate pretreatments and physical refining without the costly alkali refining step. Perhaps the savings on refining costs would cover the extra work needed to prepare the flour and to separate by centrifuging.

The high quality of crude oil from flour extraction raises a new thought about the soybean oil solvent extraction. Since it is possible to minimize the extraction of the phospholipids, free fatty acids and pigments, and to obtain a thorough extraction of triglycerides at the same time, it follows that these compounds are not mixed with triglycerides in the lipid bodies before the solvent extraction. The high phospholipid content is not inherent in soybean oil extraction. Therefore, modification of the soybean preparation procedure may be a key to producing high quality crude oil.

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