Extraction of Oil from Ground Corn Using Ethanol

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ABSTRACT: Corn oil was extracted from whole ground corn using ethanol as the solvent. The yield of oil was measured as a function of temperature, time of extraction, solvent-to-solids ratio, and ethanol concentration. Optimal conditions were a solvent-to-solids ratio of 4 mL/g corn, an ethanol concentration of 100%, 30 min of extraction time, and a temperature of 50°C. Under these conditions, a single batch extraction yielded ~3.3 g oil/100 g corn, equivalent to 70% extraction efficiency. A three-stage extraction, where the same corn was exposed to fresh ethanol, resulted in a yield of ~4.5 g/100 g corn (2.5 lb/bu of corn), equivalent to 93% recovery of the oil in corn. When anhydrous ethanol was used to repeatedly extract fresh corn, moisture was absorbed linearly by ethanol from the corn in successive stages, which, in turn, decreased oil yield and increased nonoil components in the extract.

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KEY WORDS: Corn, corn oil, dry-grind, ethanol, extraction, maize.

Currently, about 7% of the corn crop in the United States is utilized to produce ethanol by the dry-grind process. This process is widely used because of its simplicity, low capital cost, and high yield of ethanol. However, many of these processing plants are small (<60 million gallons/yr) and would be unable to survive without the help of government subsidies and tax waivers. To improve the economic viability of dry-grind ethanol plants, they should produce co-products of higher value, preferably without seriously altering the current process or lowering the value of their current products. Corn oil and proteins now pass through the dry-grind process unaltered for the most part, ending up in the by-product stream (distillers' dried grains with solubles) which is sold at low margins. If corn oil could be extracted using in-house milled corn and ethanol, it would add significant revenue without additional materials coming into the plant.

Attempts have been made in the past to develop such processes. Chen and Hoff (1), Chien *et al.* (2,3), and Hojilla-Evangelista *et al.* (4,5) first dried corn to a very low moisture content. The ethanol from fermentation of cornstarch was used to extract protein and simultaneously to extract corn oil and dehydrate the ethanol. Little residual oil remained in the defatted flaked corn, demonstrating this method's excellent oil extraction efficiency. However, some energy is required for drying the corn and for removing the ethanol from the various fractions by distillation.

The "quick germ" process attempts to remove the germ at the front end of the dry-grind process (6). The germ is recovered after whole corn is soaked in water for 3–12 h, and the germ is processed similarly to wet-milling degermination. Oil yield is about 3.1 g/100 g corn (1.75 lb/bu of corn), based on a germ oil content of 45%. This process requires the addition of moisture in the initial stages, and the end-product is still germ, thus placing the cost of processing the germ onto the buyer. In contrast, our process produces crude corn oil as the end-product rather than germ, and no additional drying or wetting of the corn is required.

The objective of this research was to optimize oil extraction from whole ground corn using ethanol as it would be practiced in a typical dry-grind ethanol plant. Corn was given no additional pretreatment (e.g., tempering, steeping, or drying). The experimental variables studied were time of extraction, concentration of ethanol in the extractant (i.e., moisture content of the ethanol), temperature of extraction, and solvent-to-solids ratio.

EXPERIMENTAL PROCEDURES

Raw materials. Milled corn was obtained from two dry-grind ethanol plants in the midwest (Chippewa Valley Ethanol Co., Benson, MN; Nebraska Energy LLC, Aurora, NE) and used without any further processing and with no screening. Whole dent corn was obtained from Anderson Grain Co. (Champaign, IL). Whole corn was ground in a Mikro-pulverizer hammer mill (Type SH; MikroPul, Summit, NJ) fitted with a 0.20-mm screen. The ground corn was used for the extraction experiments immediately after grinding. Ethanol (anhydrous, 200 proof containing 0.1–0.2% water as determined by Karl Fischer titration) was obtained from Aaper Alcohol and Chemical Co. (Shelbyville, KY). Aqueous solutions of ethanol were prepared on a vol/vol basis using deionized microfiltered water. Refined corn oil that was used as a standard in the HPLC procedure was obtained from a local grocery store.

Batch extraction. The variables studied were (i) concentration of ethanol in the extractant (% vol/vol): 70, 90, 95, 100; (ii) solvent-to-solids ratio (mL/g corn): 2, 4, 6, 8; (iii) extraction temperature (°C): 25, 50, 70; and (iv) extraction time (min): 15, 30, 120. Batch extractions were performed in 1-L Erlenmeyer flasks on a hot plate using a magnetic stir bar. The system was enclosed with aluminum foil

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and also fitted with a cold-water condenser at higher temperatures. Each extraction was carried out with 40 g of ground corn and a specified volume of the ethanol/water solvent to maintain the desired solvent-to-solids ratio (mL of solvent/g of solids). The solvent was heated to the extraction temperature before adding ground corn and stirring for the designated amount of time. The slurry was then filtered by gravity using Whatman filter paper no. 1 (11-µm mean pore size). The volume of filtrate was recorded, and samples were analyzed immediately or kept in closed bottles at 4°C.

The measured variables were oil concentration, total solids, and protein in the extract and their yields. Initially, experiments were performed by varying only extraction time. After optimal time was determined, other parameters were studied. While one parameter was kept constant (either temperature or solvent-to-solids ratio), the other two parameters were varied.

Yield of oil was expressed in two ways:

$$\text{yield (g oil/100 g corn)} = \text{concentration of oil in the extract (g/L)} \times \text{volume of extract (L/100 g corn)} \quad [1]$$

Yield was also reported as a percentage of the maximal amount of oil in corn. The maximal amount of oil from ground corn was determined by the Soxhlet method.

$$\text{yield (\%)} = \frac{\text{yield of oil (g/100 g corn)}}{\text{maximum oil in corn (g/100 g corn)}} \times 100 \quad [2]$$

The corn weight (100 g) was expressed on an "as-is" basis.

Multiple extractions. Multiple extractions were based on parameters that had been determined as optimum during the batch experiments. Two methods of multiple extraction were studied.

(i) Fresh ethanol/recycled corn. Ground corn (40 g) was extracted with 160 mL of solvent and filtered as described earlier. The filter cake (i.e., the solids retained on the filter paper) was then re-extracted with fresh absolute ethanol at the same conditions of 50°C, solvent ratio of 4 mL/g based on the initial weight of corn, and 30-min extraction time and then filtered as before. The actual weight of the filter cake fell slightly during each stage due to handling loss. However, the filter cake was re-extracted for each of the five stages, using 160 mL of fresh absolute ethanol at each stage.

(ii) Recycled ethanol/fresh corn. The filtrate from the first extraction was used to extract fresh corn. The volume of filtrate decreased in each stage because of absorption of the solvent by corn and filter paper. Typical solvent loss was 1–1.5 mL/g corn. The amount of corn for each stage was reduced to maintain the solvent-to-solids ratio at 4, thus taking solvent losses into account. This was repeated for three stages, after which the volume of liquid extract was too small for further work.

The volume of filtrate was recorded after each stage during multiple extraction. Filtrates were analyzed for oil, protein, total solids, and, in some cases, moisture content.

Proximate and sample analysis. Particle size distribution of milled corn was determined by using a rotary-screen shaker (Ro-Tap; W.S.Tyler, Inc., Mentor, OH) and U.S. standard sieves. Moisture content of the corn was determined according to AACC standard method 44-19 (7). Moisture contents of the ethanol and extracts were determined by a coulometric Karl Fischer titrator module (Denver Instrument Co., Arvada, CO). Total solids of the extracts were determined by air-drying for at least 1 h and then oven-drying at 103°C for 6 h. Nitrogen contents in the corn and the extracts were determined by Kjeldahl using AACC standard method 46-08 (7).

Oil content was determined by two methods. The Soxhlet method (AOAC 920.39C) was used initially for whole corn (8). For the extracts, an HPLC method developed in our laboratory was used (9). The columns were two 300 × 7.6-mm Phenogel SDBV columns of 5-µm and 50-Å pore size (Phenomenex, Torrance, CA) connected in series and protected by a 50 × 7.6-mm guard column of the same packing material. The mobile phase was HPLC-grade THF (Fisher Scientific, St. Louis, MO) at a flow rate of 1 mL/min at room temperature. A refractive index detector (RefractoMonitor Model IV; ThermoSeparations, Fremont, CA) was used.

Samples containing mostly oil needed little sample preparation. These samples were diluted with THF in a 1:1 ratio and filtered through a 0.2-µm syringe filter. Samples containing a significant amount of protein and other nonoil components were treated several times with hexane to extract the oil. The supernatant hexane fractions were pooled and diluted with THF in a 1:1 ratio, filtered, and then injected into the HPLC column.

Statistical analysis. The batch data for oil extraction were analyzed by Statistical Analysis Software version 8.0 (Cary, NC) with appropriate sums of squares from an analysis of variance (ANOVA) table and orthogonal polynomial contrasts of significant effects. The sums of squares for significant factors were broken down using orthogonal polynomial contrasts. The interaction of ethanol concentration and solvent-to-solids ratio was broken down into combinations of linear, quadratic, and cubic terms. The terms that did not appear to be significant were pooled into experimental error to test the significance of the other effects.

RESULTS AND DISCUSSION

Initial experiments were done with milled corn obtained from dry-grind ethanol plants. However, it appeared that storing ground corn resulted in some hydrolysis of the TG, possibly due to lipase activity. An increase in FFA was observed in the extracts when stored ground corn was used (9). Hence, in all subsequent experiments described in this paper, freshly ground corn was used.

The proximate analysis of corn showed that oil content of regular dent corn varied between 3.8 and 4.8% ("as-is") between batches, and moisture content ranged from 10.9 to 14%. Protein content (N × 6.25) averaged 8.2% ("as-is").

A particle-size analysis showed that the size of about 70% of the total weight of the sample of our milled corn was 250 µm. In contrast, dry-milled corn from operating dry-grind plants typically had larger particles, with more than 70% of

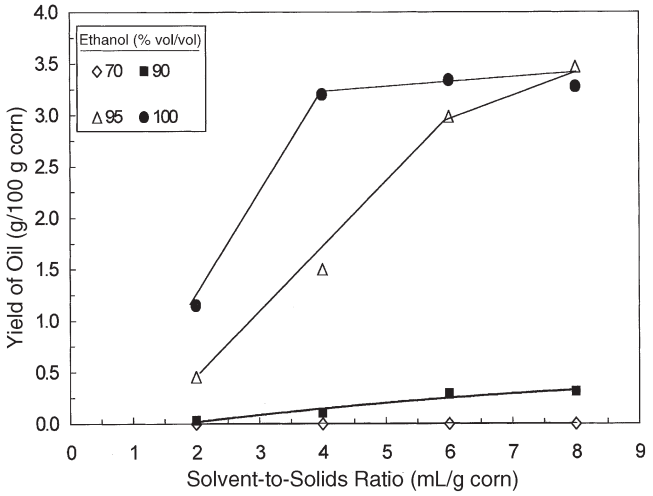

FIG. 1. Batch extraction of whole ground corn showing effect of solvent-to-solids ratio and ethanol concentration in the aqueous solvent on yield of oil in the extract. Extraction time was 30 min and temperature was 50°C.

the particles being between 200 and 800 μm (10). The smaller particle size used in our experiments should allow for better mass transfer between oil and solvent.

Batch extraction. Figures 1 and 2 show typical data obtained during batch experiments. Previous experiments (11) had determined that the optimal time of extraction was 30 min and the best temperature 50°C. Solvents with less than 95% ethanol did not extract appreciable amounts of oil, regardless of the solvent ratio. Absolute ethanol was the most effective solvent. At a solvent ratio of 4 mL/g or greater, oil yield was 3.3 g oil/100 g corn (Fig. 1), which represented an average extraction efficiency of 70%. The oil concentration in the extract was 11.1 g/L (Fig. 2). In a separate experiment (11), a solvent ratio of 10 mL absolute ethanol/g corn was used to extract the same batch of corn repeatedly. The concentration of oil in the first extract

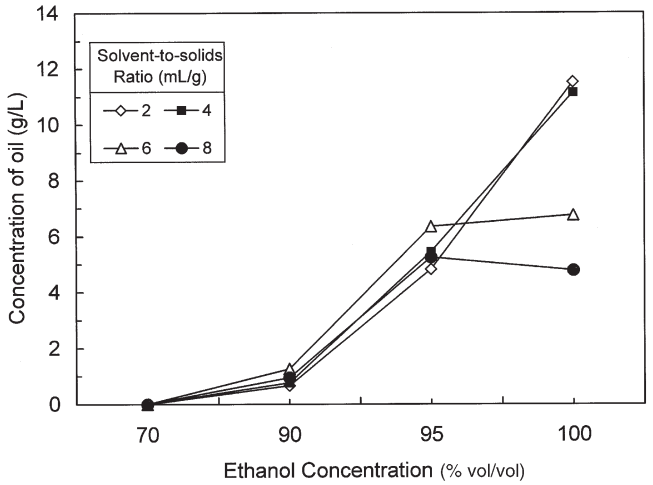

FIG. 2. Effect of solvent-to-solids ratio and ethanol concentration in the aqueous solvent on concentration of oil in the extract. Same experiments as shown in Figure 1.

was 4.2 g/L, whereas in the second extract it was 0.06 g/L. The total in the two extracts represented over 97.5% of the oil in the corn. Any further increase in the solvent ratio is not likely to increase the amount of oil extracted significantly.

On the other hand, when 95% ethanol was used, the maximal oil yield occurred at the higher ratio of 8 mL/g corn (Fig. 1). Although 95% ethanol is cheaper to produce than absolute ethanol, almost double the amount of 95% ethanol would have to be used to extract the oil from ground corn, and this could result in higher net solvent recovery costs. Lower concentrations of ethanol showed a slight upward trend as the solvent ratio increased, but the yield of oil at 90 and 70% was insignificant compared with that at the absolute and 95% concentrations. Solvents containing more than 5% water display poor extraction efficiency and low oil yield regardless of solvent-to-solids ratio, primarily due to the low solubility of oil in aqueous ethanol. This is similar to data obtained by Rao and Arnold (12), Okatame (13), and Sato *et al*. (14), which showed a drastic loss of extraction efficiency for ethanol as its moisture content increased.

The solvent-to-solids ratio makes a difference in the amount of oil extracted up to a certain point. At very high solvent-to-solids ratios, the oil simply "sees" a large bulk volume of liquid, and the limiting factor becomes the diffusive transport within the oilseed. At lower solvent-to-solids ratios, the amount of moisture in the solvent makes a difference in the solubility of the oil. Abraham *et al.* (15) suggested that the solvent-to-feed ratio had no effect on the equilibrium moisture levels and affected only the number of times the ethanol could be recycled before it reached equilibrium with the solids. When extraction time and temperature were constant, the amount of solvent had a great impact on the amount of extractable components up to a seed/solvent (wt/vol) ratio of 1:18. However, increasing the ratio increased oil yield only marginally, and there was no increase beyond the ratio 1:88 (16).

The oil concentration in the extract should be maximum to reduce solvent recovery costs. This occurred at low solvent ratios of 2–4 mL/g (Fig. 2), but this has to be balanced against the lower yields at low ratios (Fig. 1). The optimum with absolute ethanol appears to be at a solvent ratio of 4 mL/g corn.

Ethanol also extracts other nonoil components from corn. The most prominent is zein, a hydrophobic alcohol-soluble protein that is optimally extracted at 70% ethanol (10,17). Figure 3 shows the yield of protein extracted as a function of solvent ratio and ethanol concentration. Higher concentrations of ethanol, where oil becomes more soluble, extracted less protein even as more solvent was used per mass of corn extracted. Only 5–15% of the protein was extracted from the corn in a single batch extraction with 95 or 100% ethanol. Zein constitutes about 40% of the protein in corn (10,17).

Figure 4 summarizes the extraction parameters for batch extraction at a solvent-to-solids ratio of 4 mL/g corn, temperature of 50°C, and extraction time of 30 min. Under these conditions, absolute ethanol yields the maximal amount of oil, about 3.2 g of oil/100 g of corn. The extraction of nonoil components (estimated as total solids minus the oil shown in

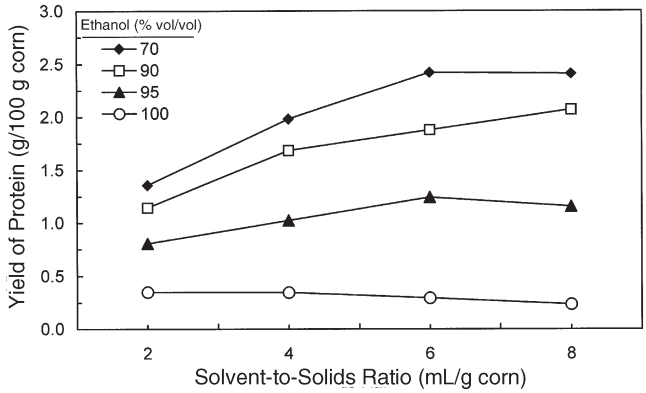

FIG. 3. Effect of solvent-to-solids ratio and ethanol concentration on yield of protein in the extract. Same experiments as shown in Figure 1.

Fig. 4) increased as the ethanol concentration decreased. Not all the nonoil components could be attributed to protein (zein). The total solids extracted overall did not change drastically as the ethanol concentration was varied, showing a trade-off between oil and protein as the extractable components.

The batch experiments were analyzed statistically. The main effects of the parameters examined were approximated by inspection of the data. The interaction effect of ethanol concentration and solvent-to-solids ratio was determined to be significant at $P < 0.05$ (11) and further analyzed statistically. The breakdown of the interaction of solvent-to-solids ratio and concentration of ethanol using orthogonal polynomial contrasts enabled greater comprehension of this interaction. The calculations of the sums of squares and effects for each of the terms are summarized in the ANOVA (Table 1). The portions of the interaction that contained the linear effect of solvent-to-solids ratio were significant, containing a large amount of the total sums of squares. This suggests that the effect of the solvent, as described by its volume in relation to the amount of solids and the amount of moisture present, is primarily linear.

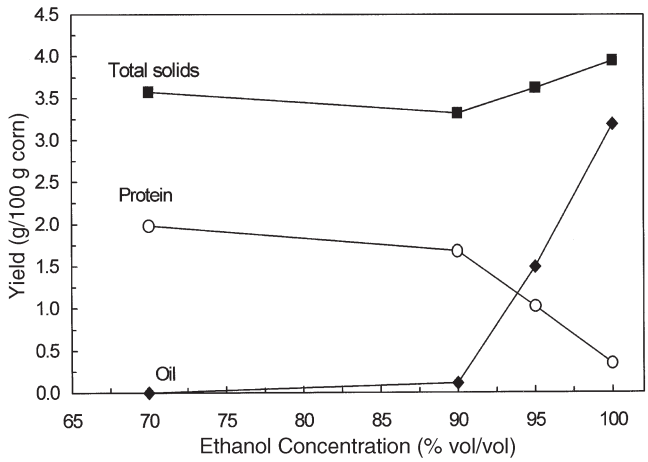

FIG. 4. Batch-extraction data showing effect of ethanol concentration on yield of oil, protein, and total solids. Extraction time was 30 min, temperature was 50°C, and solvent-to-solids ratio was 4 mL/g corn.

TABLE 1
ANOVA Table with Effects Broken Down with Orthogonal Polynomial Contrasts[a,b]

Source of variation	DF	Sum of squares	Mean square	*F*
Total	23	7.86	0.34	7.95
Ethanol	3	1.42	0.47	10.99
E linear	1	2.43	2.43	56.50
E quad	1	1.00	1.00	23.26
E cubic	1	0.38	0.38	8.84
Solvent ratio	3	0.73	0.24	5.64
R linear	1	0.71	0.71	16.56
R quad	1	0.00	0.00	0.03
R cubic	1	0.01	0.01	0.23
Ethanol × ratio	9	0.74	0.08	1.91
E lin x R lin	1	0.41	0.41	9.44
E lin x R quad	1	0.00	0.00	0.00
E lin x R cub	1	0.00	0.00	0.01
E quad x R lin	1	0.07	0.07	1.57
E quad x R quad*	1	0.02	0.02	
E quad x R cub*	1	0.01	0.01	
E cub x R lin	1	0.26	0.26	6.11
E cub x R quad*	1	0.14	0.14	
E cub x R cub*	1	0.01	0.01	
Error (pooled)	4	0.17	0.043	

[a]E, ethanol concentration; R, solvent ratio; lin, linear; quad, quadratic; cub, cubic.
[b]Terms with asterisks were pooled into the error.

Only the linear term of ethanol concentration, combined with the linear term of the solvent-to-solids ratio, showed significance with respect to ethanol concentration. All other higher-order terms for ethanol concentration were nonsignificant. The higher-order polynomial terms were pooled into an error term and used to test the terms containing linear contrasts (Table 1). The pooled error term was greater than the variance obtained in replicated experiments (11) but still considerably less than the other terms that had a significant effect within this data set. Therefore, the use of the pooled error term should not lead to any false deduction of significance of any of the terms, which would be a type I error (concluding that the two results are different when they are not).

Multiple-batch extractions. The purpose of multiple-batch extractions was to simulate continuous extraction and to maximize the yield of oil from the ground corn. Figures 5 and 6 show experiments in which the solvent was recycled with fresh corn in each successive stage. Oil concentration dropped in each successive stage whereas the total solids concentration increased (Fig. 5). The moisture in the fresh corn was transferred to the ethanol solvent in each stage. This resulted in moisture increasing from 0.16% in the fresh ethanol to 4.36% in the third-stage extract. The moisture increase partly explains the increase in nonoil solids extracted (Fig. 5) as well as the decreasing yield of oil and total solids in each consecutive stage (Fig. 6). As with solvent-to-solids ratio, a point of diminishing returns is reached after several extractions. The oil yield for the third stage (which used recycled ethanol containing 4.36% moisture) was consistent with data obtained earlier for a single-batch extraction using 95% ethanol (Fig. 2). It

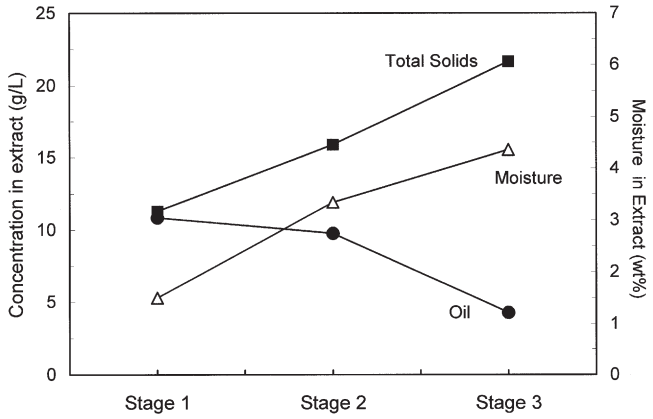

FIG. 5. Concentration profiles of total solids, oil, and moisture in the extract during multiple-stage extraction with fresh corn using recycled ethanol in each stage. Absolute ethanol (0.16% moisture) was used in the first stage. Solvent-to-solids ratio was 4 mL/g corn in each stage. Temperature was 50°C, and extraction time was 30 min in all stages.

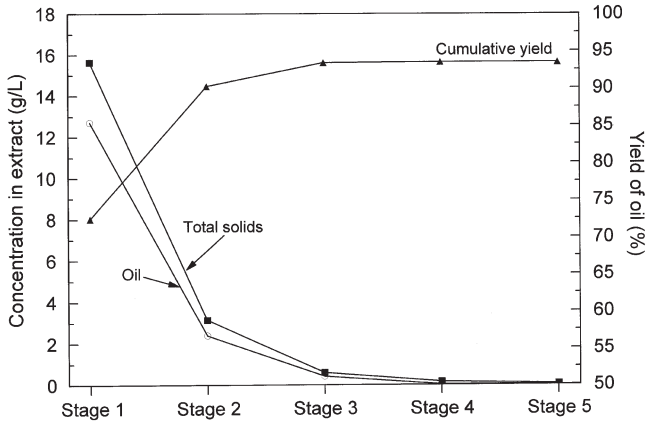

FIG. 7. Multiple-batch extraction using recycled corn and fresh ethanol. Absolute ethanol was used in each stage. Solvent-to-solids ratio was 4 mL/g corn, temperature was 50ºC, and extraction time was 30 min.

is clear from Figure 6 that the extraction efficiency of the solvent for oil decreases significantly after the first stage. The greater proportion of nonoil solids in the later stages will make subsequent refining of the corn oil more difficult.

Work by Hron and Koltun (18) showed that after fifteen 10-min extractions, the residual lipids in the oilseed residue could not be reduced below 2% without washing or below 1% without pressing because of the lipidlike material soluble in petroleum ether in the recycled miscella. However, in general, multiple extractions and washing with solvent is an effective way to remove a majority of the lipids by batch extraction.

With the other mode of multiple extraction, the same batch of corn was extracted repeatedly with fresh volumes of ethanol. As shown in Figure 7, the amount of oil extracted decreased dramatically after the first stage. The cumulative yield leveled off after the third stage to about 93% of the oil extracted in this mode of operation. Our experience with the multiple-batch extractions indicated that the optimal mode of extraction may be a combination of countercurrent and cocurrent flow of solvent and ground corn.

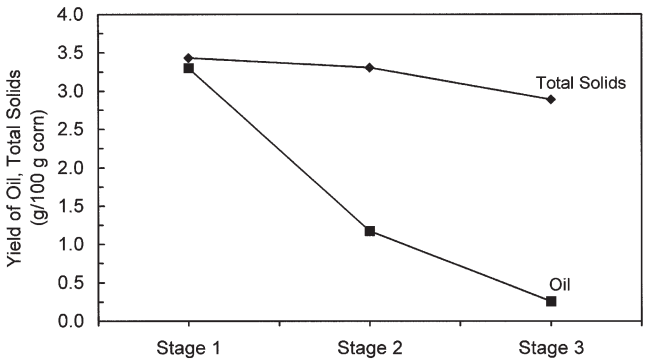

FIG. 6. Yield of oil and total solids during multiple-batch extraction with fresh corn and recycled ethanol in each stage. Same experiment as shown in Figure 5.

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