Pilot-Scale Two-Phase Extraction of Canola

Mahmood Thobani and Levente L. Diosady*

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, M5S 3E5, Canada

ABSTRACT: An extraction process was developed in our laboratory for rapeseed (canola) with 10% (w/w) ammonia in methanol, containing 5% (vol/vol) water, and hexane to simultaneously produce an improved meal and a high-quality oil. To remove the hazards associated with the use of ammonia, a two-phase solvent extraction, with 0.08% (w/w) sodium hydroxide replacing the ammonia, was tested on a semipilot scale with a Szego mill and a Karr reciprocating-plate extraction column. Flooding curves and appropriate agitation parameters were examined for this system. Then, the effects of polar solvent-to-seed ratio, slurry-to-hexane flow ratio, plate amplitude and plate agitation frequency on extraction efficiency were investigated. The process is technically viable for industrial application. A meal that contained 0.9% residual oil, 44.4% protein and 2.79 mmol/kg glucosinolates (moisture and oil-free basis) and a miscella with 19.5% oil were obtained.

JAOCS 74, 201–206 (1997).

KEY WORDS: Canola meal, canola oil, canola seed, extraction, glucosinolates, hydrodynamics, Karr column, Szego mill.

Rapeseed is Canada's most important oilseed crop. It contains 40–45% oil and 22–24% protein. Canada, the world's third largest rapeseed producer, accounts for about 14% of the total supply of 26 million metric tons (1). Canadian rapeseed production consists mainly of "canola" varieties, which are low in both erucic acid and glucosinolates.

Canola oil is characterized by a low level of saturated fatty acids. The defatted meal contains about 38% protein (at *ca.* 8% moisture) and is mainly used as a feed supplement for livestock and poultry. Although the meal protein has a well-balanced amino acid composition (2), its use as a food-protein source is limited by the presence of undesirable components, such as glucosinolates, phenols, phytates, and high fiber content.

Our laboratory developed a unique process in which canola is simultaneously contacted by two immiscible solvents to produce an improved meal and a high-quality oil (3,4). Methanol with 5% (vol/vol) water and 10% (w/w) ammonia is used as a polar phase and hexane as a nonpolar phase. The methanol inactivates myrosinase and removes most of the hydratable phospholipids, resulting in improved oil quality. The meal thus produced is high in protein content (about 50%), light in color, free flowing and bland in taste. It is free of glucosinolates and low in phenolics. The oil is essentially free of phospholipids and does not contain significant amounts of sulfur-containing compounds.

The process was tested on a semipilot scale with a Szego mill (General Comminution Inc., Toronto, Ontario, Canada) and a Karr reciprocating-plate column (Pegasus Industrial Specialties Ltd., Toronto, Ontario, Canada) (5,6). The Szego mill, an orbital mill developed at the University of Toronto, is compact and has a high throughput, moderate energy consumption, and low cost (7). It is effective for slurry grinding and glucosinolate extraction. The Karr column was used as a countercurrent slurry-liquid contactor for oil extraction. It has a high volumetric efficiency and is able to handle suspended solids. In addition, it has a low cost and low maintenance (8).

Because ammonia is a toxic gas, its containment is an important and expensive consideration in the application of the process. A less volatile replacement would make the process more practical. Also, the solubility of NH_3 in the CH_3OH phase decreases with increasing temperature, and the NH_3 extraction must therefore be carried out at a relatively low temperature, which lowers extraction efficiency. The objective of this study was to test the feasibility of replacing NH_3 with 0.08% (w/w) NaOH in the polar phase. Effects of polar solvent-to-seed ratio, slurry-to-hexane flow ratio, plate amplitude, and plate agitation frequency on extraction efficiency were investigated. Effects of different operating variables on hold-up, in the absence of mass transfer, were first investigated to determine flexibility, operating range, and appropriate agitation parameters for our CH_3OH/H_2O–hexane system.

MATERIALS AND METHODS

Materials. Canola seed (mixture of Global, Delta, and Triton cultivars) was obtained through the courtesy of CanAmera Foods (Hamilton, Ontario, Canada). The chemical composition, expressed on a dry basis, was 46.4 ± 0.2% oil; 22.8 ± 0.8% protein; and 8.43 ± 0.65 µmol glucosinolates per gram of meal. Technical-grade methanol and hexane were obtained from Canada Colors and Chemicals Ltd. (Toronto, Ontario, Canada). Anhydrous ammonia and 50% (w/w) NaOH (aq) were obtained from Canadian Liquid Air Ltd. (Montreal, Québec, Canada) and BDH Inc. (Toronto, Ontario, Canada), respectively. All chemicals used for analyti-

---

*To whom correspondence should be addressed.

cal work were reagent-grade and obtained from major chemical suppliers.

The Szego mill, an orbital mill, consists of a stationary vertical cylinder (stator) in which three helically grooved rollers rotate on flexible shafts. The feed is crushed between the rollers and the stator. It had the following dimensions: stator diameter, 100 mm; roller diameter, 39 mm; roller length, 170 mm; roller groove width, 2 mm; groove, 4 mm.

The Karr reciprocating-plate extraction column consisted of a shell that enclosed a vertically reciprocating plate assembly, consisting of a number of perforated plates. It had the following dimensions and materials of construction: diameter 0.05 m; overall height, 3.3 m; effective extraction height, 2.5 m; number of plates, 82; plate spacing, 0.025 m; shell material, glass; and plate material, teflon.

The $CH_3OH/H_2O/NH_3$ solution was prepared by bubbling anhydrous ammonia through methanol that contained 5% (vol/vol) water, at 0°C. The quantity of dissolved ammonia was determined by titrating with 0.1 N H_2SO_4. The solution was made up to the required ammonia content (10% w/w) by dilution with ammonia-free solvent. The $CH_3OH/NaOH/H_2O$ solution was prepared by adding 50% (w/w) NaOH (aq) to 95/5% (vol/vol) methanol/water to make a 0.08% (w/w) NaOH solution.

Analytical methods. Moisture contents were determined gravimetrically. Samples were dried to constant weight at 110°C in a forced-air oven (9). The oil content was determined with a Soxhlet apparatus. Ground seed and treated meal samples were extracted with hexane for 24 and 12 h, respectively (10). The crude protein content (as N · 6.25) was determined by the Kjeldahl method (11) by using Buchi digestion and distillation modules (Laboratoriums Technik AG, Flawil, Switzerland). The residual glucosinolates and their breakdown products were determined according to the method of Wetter and Youngs (12), based on the ultraviolet absorbance of the glucosinolate hydrolysis products, thioureas and oxazolidine-2-thione.

During extraction test runs, the residual oil content of the meal was determined by further hexane extraction in a Soxhlet apparatus. The volume fraction of miscella in the filtrate, the miscella entrainment, was also measured. The polar phase was reextracted three times with hexane at a polar phase-to-combined hexane ratio of one (vol/vol) to determine its oil content. Oil and gum contents in the miscella and polar phase, respectively, were determined by evaporating the solvents under vacuum in a rotary evaporator.

Karr column hydrodynamics. CH_3OH/H_2O [95/5% (vol/vol)] and hexane were pumped into the top and bottom of the column, respectively. The column was operated at room temperature, with CH_3OH/H_2O as the continuous phase. The interface level was maintained at the top of the column, just below the CH_3OH/H_2O inlet, by manually controlling the flow rate of polar slurry with the exit valve at the bottom of the column. For each run, the column was brought to steady state after four effective volumes of the column were displaced by the combined flows.

The effect of plate agitation frequency (s^{-1}) and total throughput (L/min; sum of the dispersed and continuous phase flow rates into the column) on hold-up (volume fraction of the column occupied by the hexane phase) was investigated. Total throughput and flow ratio were kept constant (CH_3OH/H_2O-to-hexane flow ratio = 2, stroke length = 3.7 cm). The hold-up was measured at steady state at different plate frequencies until flooding was observed. This was repeated at different total throughputs while maintaining the same flow ratio.

The effect of plate amplitude [half-stroke length (cm)] and plate agitation frequency were considered as two independent variables. Hold-up was measured at steady state over a wide range of degrees of agitation, defined as the product of plate amplitude and plate agitation frequency. At each agitation degree, the hold-up was measured at both low amplitude and high frequency, and high amplitude and low frequency.

Semipilot-scale extraction. Figure 1 is a flowsheet for the semipilot-scale extraction process used. Several experiments with different operating conditions were carried out to investigate the effects of plate amplitude, plate agitation frequency, flow ratios, and solvent-to-seed ratios.

For each run, canola seed (8 or 10 kg) and $CH_3OH/H_2O/$ NaOH at a solvent-to-seed (R) ratio of 2.5 (vol/wt) were manually fed into the Szego mill. The ground slurry was collected and reground. The twice-ground slurry was then diluted with more $CH_3OH/H_2O/NaOH$ to $R = 5.7$ or 6.7 (vol/vol) and transferred into a feed tank. The contents were continuously agitated to maintain a uniform distribution of solids in the polar solvent. The slurry was then pumped into the top of the column with a progressing cavity pump (Moyno pump; Robbins and Myers Ltd., Brampton, Ontario, Canada), and hexane was pumped into the bottom of the column with a constant-volume diaphragm pump (metering pump). The column was operated with the slurry as the continuous phase.

During each run, samples of slurry and miscella, exiting the bottom and top of the column, respectively, were taken every few minutes for later analysis. The slurry sample was vacuum-filtered through Whatman No. 41 filter paper (Maidstone, England). The meal residue was rinsed three times with methanol, each time at an approximate solvent-to-meal ratio of 3.5 (vol/wt), and air-dried overnight.

At the end of each run, the raffinate phase (slurry) was vacuum-filtered through Whatman No. 1 filter paper to separate the meal residue from the polar solvent. Oil and gum were recovered from the extract (miscella) and the polar solvent, respectively, by evaporating the solvents in a rotary vacuum evaporator and a 20-L batch distillation unit.

The pilot-scale tests were limited by solvent recovery capacity. Two runs were repeated, to assure that the process was reproducible; however, the repetition of all runs was not possible due to cost and time constraints. As mentioned earlier, several samples were taken during the steady-state runs, and these were individually analyzed. At steady state, the oil concentration in the miscella remained constant for 4–6 samples with a relative standard deviation of <5%.

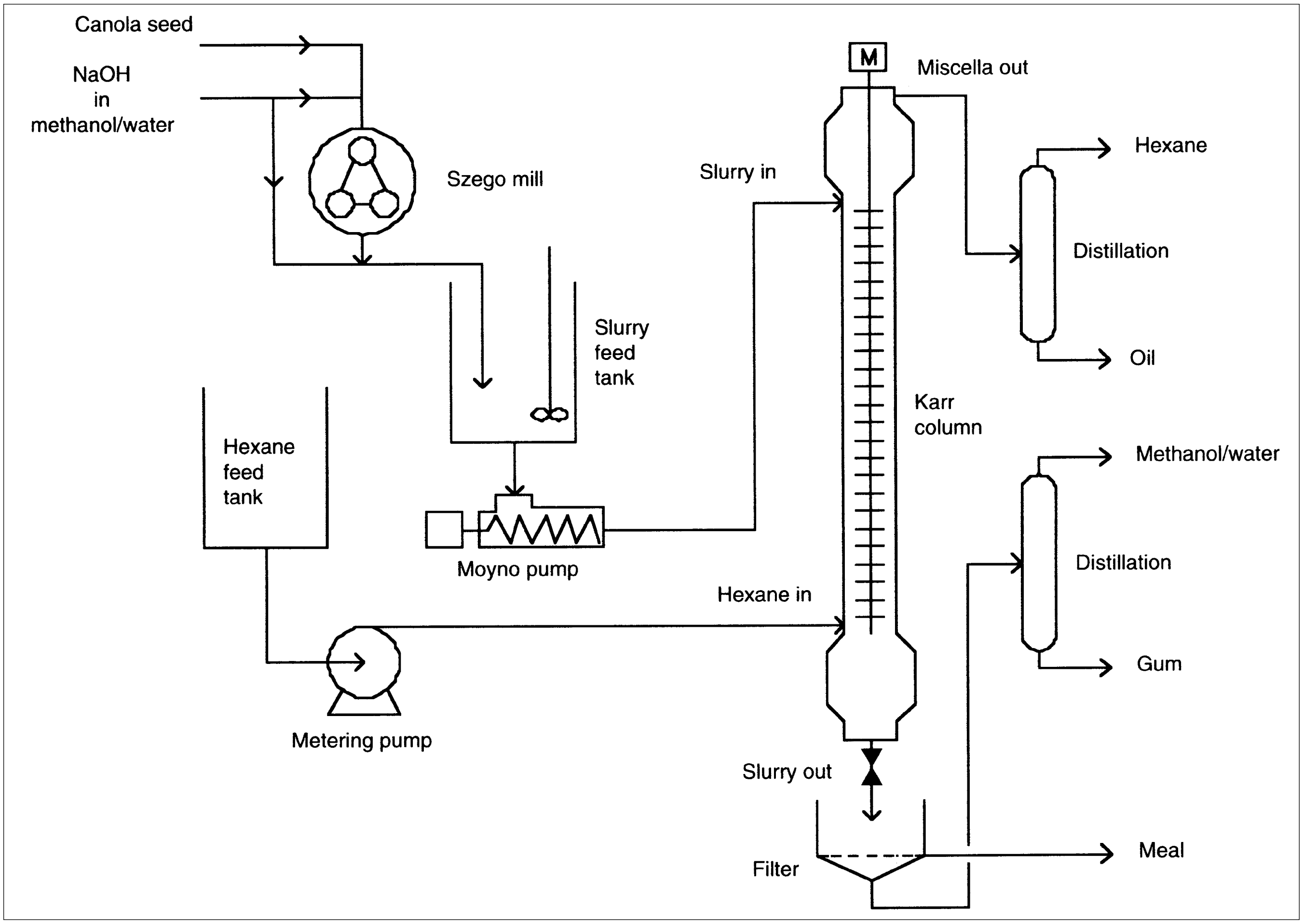

FIG. 1. Flowsheet of the two-phase solvent extraction process. Szego Mill (General Comminution Inc., Toronto, Ontario, Canada); Karr column (Pegasus Industrial Specialties Ltd., Toronto, Ontario, Canada); Moyno pump (Robbins and Myers Ltd., Brampton, Ontario, Canada).

RESULTS AND DISCUSSION

Karr column hydrodynamics. Hold-up is an important variable in extraction columns. A higher hold-up is a result of greater specific interfacial area and should in turn result in improved mass transfer. In these experiments, hold-up increased as the flow rates increased at constant agitation, or by increased agitation at constant flow rates (Fig. 2). However, flooding imposed a limit on the agitation level that could be used. Flooding was identified by the formation of an emulsion near the middle of the column and the formation of a second interface below the hexane inlet. Eventually, hexane began to leave with the CH_3OH/H_2O. Flooding also would be expected to impose a limit on the flow rates that can be used. At higher total throughput, the column flooded at lower agitation.

The Karr column was stable at total throughputs of 51, 76, and 102 mL/min/cm^2 up to agitation levels of 72, 66, and 40 cycles/min, respectively. The flooding points lie somewhere along the dotted lines (Fig. 2).

Baird *et al.* (13) showed that agitation degree, which is the product of plate amplitude and plate agitation frequency, is the correct agitation parameter for Karr columns. Hafez and Baird (14) and Baird and Shen (15) later raised questions about using the product as a single agitation variable at high frequencies and low amplitudes. Baird and Lane's experiments were also carried out at amplitudes and frequencies much higher than those likely to be encountered in our system. An investigation to determine the appropriate agitation parameter for our system was therefore necessary (Table 1).

Statistical analysis (independent *t*-test) indicated that, at constant $A \cdot f$, the hold-up was constant (98% significance level) for each of the $A \cdot f$ values tested (Table 1). The product of amplitude and frequency may thus be considered as a single agitation variable in this system. The hydrodynamic data, although obtained in a simpler liquid-liquid system, allowed us to predict and regulate the behavior of the slurry–liquid system.

Semipilot-scale extraction. In the column, the two phases traveled countercurrently due to their different densities. As hexane traveled up the column, it extracted the oil, and the extract (miscella) exited from the top of the column. The depleted raffinate stream exited from the bottom of the column. Plate agitation created and maintained dispersion and pro-

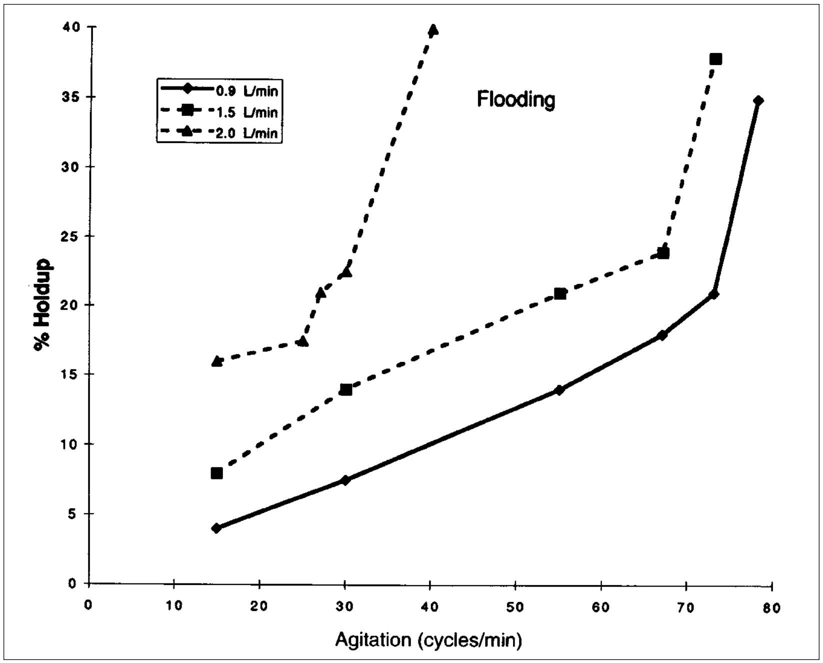

FIG. 2. Effect of plate agitation and total throughput on holdup.

moted mass transfer. A concentration gradient provided the necessary driving force for mass transfer. The mechanism of oil extraction involved the transfer of oil from the solid into the methanol phase (continuous phase) and finally into the hexane phase (dispersed phase). The meal was suspended in the methanol phase because the meal was closer in density to the methanol phase than to the hexane phase. The surface tension of methanol also ensured that the meal was retained in the methanol phase.

Figure 3 shows typical oil concentration profiles in the miscella and meal as a function of time for one run. The system required approximately 40 min to reach steady state. Each run was therefore carried out for at least 60 min. The extraction results are presented in Table 3.

The effect of plate amplitude and plate agitation on oil extraction was investigated in runs 1 and 2 (Table 2). The runs were performed at high amplitude and low agitation (run 1) and vice versa (run 2), while keeping the degree of agitation and other parameters constant. The results were almost the same. The product of amplitude and frequency as a single agitation variable therefore appeared to be the appropriate agitation parameter, even for the solid-liquid-liquid extraction system.

TABLE 1
Effects of Plate Amplitude and Plate Agitation Frequency on Holdup[a]

Run	Amplitude[b] (cm)	Agitation frequency (s^{-1})	Agitation degree[c] (cm/s)	% Holdup (vol/vol)
A	1.8	0.33	0.59	10.4 ± 0.5
B	0.3	1.93	0.58	9.6 ± 0.5
C	1.8	0.92	1.66	18.3 ± 1.2
D	0.8	2.12	1.70	15.3 ± 1.0

[a] Total throughput = 1.5 L/min; CH_3OH/H_2O-to-hexane flow ratio = 2.
[b] Half-stroke length (cm).
[c] Amplitude × frequency.

The effect of the slurry-to-hexane flow ratio on oil extraction was studied in runs 3 and 4. A flow ratio of 2.3 resulted in a miscella oil content of 38% and a meal oil content of 8.3%. A lower flow ratio of 1.7 gave more satisfactory results: 18.8 and 3.8% oil contents in the miscella and meal, respectively. Although a lower flow ratio resulted in better mass transfer, the energy costs for the separation of oil and hexane are higher because of the lower oil concentration in the miscella. A compromise between the two must be selected. At higher flow ratio, the higher miscella oil concentration reduced the concentration driving force for mass transfer and

TABLE 2
Semipilot-Scale Extraction: Operating Conditions

Run number	Solvent-to-seed ratio (L/kg)	Slurry flow rate (L/min)	Hexane flow rate (L/min)	Stroke length (cm)	Agitation frequency (cycles/min)
1	6.7	0.65	0.35	3.5	50
2	6.7	0.65	0.35	2.7	65
3	6.7	0.95	0.42	3.7	50
4	6.7	0.85	0.50	3.7	50
5	6.7	0.50	0.45	3.7	65
6	6.7	0.85	0.50	3.7	65
7	6.7	0.85	0.50	3.7	75
8	5.7	0.50	0.45	3.7	65
9	5.7	0.50	0.45	3.7	65
10	5.7	0.50	0.45	3.7	72

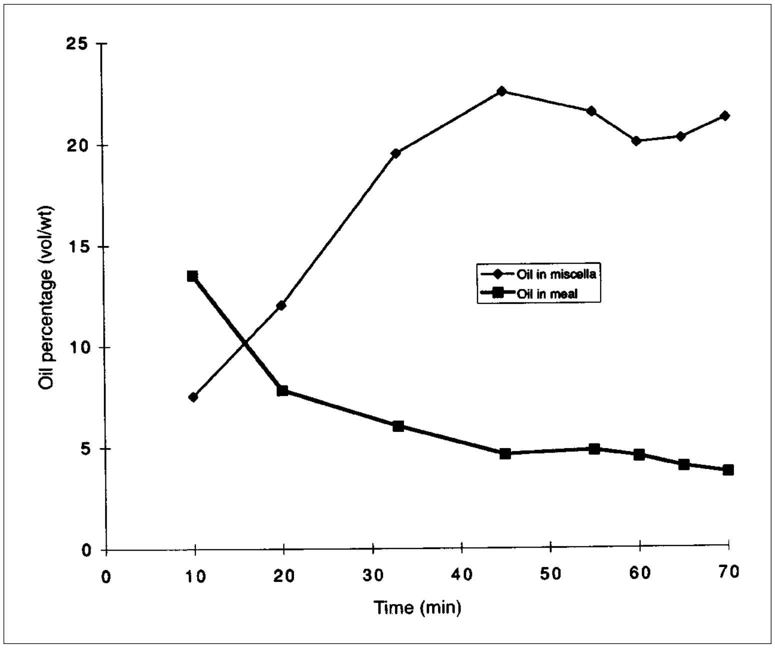

FIG. 3. Typical oil concentration profile (run 1).

resulted in less oil extraction. The higher viscosity of the miscella stream also likely increased resistance to mass transfer. However, this could be compensated for by a higher column.

The effect of $CH_3OH/H_2O/NaOH$-to-seed ratio (vol/wt) (R) on the oil extraction was also examined (runs 5, 8, and 9). Runs 8 and 9 were carried out with identical operating conditions to check reproducibility of the extraction results. Surprisingly, a higher R gave less satisfactory results in terms of oil extraction. At constant slurry and hexane flow rates into the column, a higher R in the slurry feed into the column meant a higher hexane-to-seed contact ratio in the column itself. Improved mass transfer was therefore expected. However, due to the low oil concentration in the miscella, a relatively large density difference between the two countercurrent streams probably resulted in less intimate contact between the two streams and, therefore, less efficient mass transfer.

The effect of plate agitation on the oil extraction was explored at $R = 5.7$ and 6.7 (runs 4, 6, and 7; runs 8, 9, and 10). As expected, a higher agitation resulted in improved mass transfer, leading to lower oil contents in the meal and correspondingly higher oil contents in the miscella. At $R = 6.7$, increasing the agitation from 50 to 65 cycles/min reduced the oil content in the meal by 13% from 3.8 to 3.3%. Increasing the agitation to 75 cycles/min resulted in flooding. Flooding was identified by increasing miscella holdup in the column and its subsequent exit, with the depleted slurry, from the bottom of the column. At $R = 5.7$, increasing agitation from 65 to 72 cycles/min significantly reduced the oil content in the meal from 2.1 (mean of runs 8 and 9) to 0.9%; 72 cycles/min was close to the upper limit of agitation imposed by flooding (Fig. 2). Maximum extraction is expected just below the flooding point.

Table 3
Semipilot-Scale Extraction: Results

Run number	Oil in miscella % (wt/vol)	Oil in meal % (w/w)	Protein content of meal (%)	Glucosinolate content of meal (µmol/g)	Entrained miscella % (vol/vol)	Oil in MeOH phase % (w/w)	Gum in MeOH phase % (w/w)	NTS[a]
1	20.5	4.2	43.1	2.61	12.6	n.d.[b]	n.d.	1.6
2	22.0	4.0	46.0	3.28	n.d.	n.d.	n.d.	1.7
3	38.0	8.3	39.6	3.63	10.2	0.21	1.4	1.8
4	18.8	3.8	40.3	3.55	n.d.	0.26	1.5	1.6
5	11.2	3.1	42.7	2.48	7.6	0.08	1.5	1.4
6	21.1	3.3	41.0	3.66	10.3	0.20	1.6	1.7
7	F[c]	F	F	F	F	F	F	F
8	16.4	2.0	40.5	3.66	10.9	0.14	1.7	1.8
9	14.9	2.2	39.9	3.58	11.7	0.12	1.7	1.7
10	19.5	0.9	44.4	2.79	14.2	0.13	1.9	3.1

[a] NTS, Number of theoretical stages. [b] n.d., Not determined. [c] F, Flooding.

The crude protein contents of the column-extracted meals ranged from 39.6 to 46.0%. Use of a taller column would result in lower residual oil and higher protein content in the meal. Increased protein loss into the methanol phase may have occurred as a result of the considerable time elapsed between shutting down (clean up, etc.) of the Szego mill grinding operation, transferring of materials from one location to another, and starting up of the subsequent Karr column extraction. A continuous operation would reduce protein loss.

The glucosinolate contents of the oil-free meals ranged from 2.48 to 3.66 μmol/g, which corresponds to 70.6 to 56.6% extraction, respectively, of the glucosinolates originally present in the seed. R had the most obvious effect on glucosinolate extraction. Higher R improved the extraction. $R = 5.7$ and $R = 6.7$ resulted in 57.0 (mean of runs 8 and 9) and 70.6% removal, respectively, of the glucosinolates originally present in the seed.

The oil contents in the polar phase were <0.3% (wt/vol). The partition of oil in the two solvent phases resulted in little oil dissolving in the polar phase. The gum content in the polar phase ranged from 1.4 to 1.9% (wt/vol). Significant amounts of miscella, ranging from 7.6 to 14.2% (volume miscella/volume solid-free methanol phase), were found entrained in the exiting slurry. Miscella entrainment reduced concentration gradients and, therefore, mass transfer efficiency.

The number of theoretical stages ranged from 1.4 to 3.1, corresponding to a height equivalent of a theoretical stage of 1.8 to 0.80 m, respectively.

Run 10 gave the best overall results from the point of view of oil contents in the meal and miscella, and protein and glucosinolate contents of the meal. The oil values are comparable to those produced in conventional oilseed extractors. Higher protein and significantly lower glucosinolate contents of the meals were also obtained compared to conventional hexane-extracted meals. As for semipilot-scale $CH_3OH/H_2O/NH_3$ extraction, results were better than those obtained in benchtop tests (16). Much lower oil and glucosinolate contents in the meal were obtained. Szego mill grinding produced flake-shaped particles, which improved mass transfer. Countercurrent flow in the Karr column provided a greater number of contacting stages and resulted in more efficient oil extraction.

Semipilot-scale tests with NH_3 under similar conditions (17) produced better results. Lower oil and glucosinolate, and higher protein contents in the meal were obtained. The lower oil recovery with NaOH may be due to saponification of triglycerides by NaOH.

Although NaOH was not as effective as NH_3, it makes the process attractive in some situations. The use of NaOH makes solvent preparation and recovery easier and less costly, and it eliminates potential exposure to ammonia, which is a toxic gas.

The results indicate that the commercial application of the two-phase solvent extraction process should be investigated. The equipment is smaller and less expensive than that used in conventional extraction plants, and the energy requirements and operating costs are expected to be similar. Energy savings in the flaking and cooking steps are likely to be sufficient to offset the cost of recovering the second solvent.

ACKNOWLEDGMENTS

Financial assistance of NSERC and MRCO is gratefully acknowledged. The authors thank Stephan Reynier and Vincent Loo for their technical assistance.

REFERENCES

1. Anonymous, Fats and Oils in Canada, *Annual Review,* External Affairs Canada, Ottawa, 1992.
2. Ohlson, R., and K. Anjou, Rapeseed Protein Products, *J. Am. Oil. Chem. Soc. 56*:431–437 (1979).
3. Rubin, L.J., L.L. Diosady, and C.R. Phillips, Solvent Extraction of Oil Bearing Seeds, U.S. Patent 4 460 504 (1984).
4. Rubin, L.J., L.L Diosady, M. Naczk, and M. Halfani. The Alkanol–Ammonia–Water/Hexane Treatment of Canola, *Can. Inst. Food Sci. Technol. J. 19*:57–61 (1986).
5. Diosady, L.L., C.G. Tar, L.J. Rubin, and M. Naczk, Scale-Up of the Production of Glucosinolate Free Meal, *Acta Alimentaria 16*:167–179 (1987).
6. Diosady, L.L., L.J. Rubin, and C.G. Tar, Extraction of Particulate Materials, U.S. Patent 4 859 371 (1989).
7. Trass, O., The Szego Grinding Mill, in *Proceedings of International Symposium on Fine Particle Processing,* Society of Mining Engineers, AIME, edited by Somasundaram, Las Vegas, Vol. 1, pp. 96–112 (1980).
8. Karr, A.E., Design, Scale-Up and Applications of the Reciprocating Plate Extraction Column, *Sepn. Sci. Technol. 15(4)*:877–905 (1980).
9. *Approved Methods of the American Association of Cereal Chemists,* American Association of Cereal Chemists, Inc., St. Paul, 1976, Method 44-15A.
10. *Official Methods and Recommended Practices of the American Oil Chemists' Society,* Champaign, 1980, Method Ba 3-38.
11. *Approved Methods of the American Association of Cereal Chemists,* American Association of Cereal Chemists, Inc., St. Paul, 1976, Method 46-12.
12. Wetter, L.R., and C.G. Youngs, A Thiourea–UV Assay for Total Glucosinolate Content in Rapeseed Meals, *J. Am. Oil Chem. Soc. 53*:162–164 (1976).
13. Baird, M.H.I., G.C. McGinnis, and G.C. Tan, Flooding Conditions in a Reciprocating-Plate Extraction Column, in *Proceedings International Solvent Extraction Conference (ISEC 71),* The Hague, Society of Chemical Industrialists, London, 1971, pp. 251–259.
14. Hafez, M.M., and M.H.I. Baird, Power Consumption in a Reciprocating Plate Column, *Trans. Instn. Chem. Engrs. 56*:229–238 (1978).
15. Baird, M.H.I., and Z.J. Shen, Holdup and Flooding in Reciprocating Plate Extraction Columns, *Can. J. Chem. Eng. 62*:218–227 (1984).
16. Thobani, M., and L.L Diosady, Two-Phase Solvent Extraction of Canola, *J. Am. Oil Chem. Soc. 74*:207–214 (1997).
17. Liu, J., M. Shi, L.L. Diosady, and L.J. Rubin, Three-Phase Extraction of Chinese Rapeseed Using the Karr Column, *J. Food Eng. 24*:35–45 (1995).

[Received October 2, 1995; accepted November 21, 1996]