Recovery of Corn Oil from Ethanol Extracts of Ground Corn Using Membrane Technology

Jason R. Kwiatkowski[a,*] and Munir Cheryan[a,b]

University of Illinois, Departments of [a]Agricultural and Biological Engineering and [b]Food Science and Human Nutrition, Agricultural Bioprocess Laboratory, Urbana, Illinois 61801

ABSTRACT: The recovery of additional co-products from the dry-grind process for ethanol could influence the industry greatly, as most facilities today rely on subsidies and tax incentives to operate. Modification of the process to include the extraction of oil could add $0.30–0.50 per bushel to the value derived from corn. A process combining solvent extraction with membrane technology to recover the oil was investigated. To evaluate the feasibility of this process, several nanofiltration membranes were tested for their stability in ethanol. Each of the membranes was conditioned with a solution of water/ethanol (0–100 vol/vol%) and the top three were chosen based on their performance with respect to flux and rejection. Beginning at 5 g/L, solutions of corn oil in ethanol were concentrated to over 100 g/L with the DK (Osmonics-Desal, Minnetonka, MN), TFC-SR1 (Koch Membrane Systems, Inc., Wilmington, MA), and TFC-SR2 (Koch) membranes. The liquid extract was then similarly concentrated, yielding a retentate fraction that was highly concentrated with solids in addition to corn oil, such as protein (zein), lecithins, and other potentially high-value fractions soluble in ethanol. Analysis of the extract retentate showed a significant increase in oil concentration with an increase in the volume concentration ratio, indicating that pure ethanol extracts from corn may be successfully concentrated using nanofiltration membranes.

Paper no. J10997 in *JAOCS 82*, 221–227 (March 2005).

KEY WORDS: Corn oil, dry-grind, ethanol, membrane, nanofiltration, nonaqueous.

Corn oil is one of the most valuable components of the corn kernel, on a per ton basis. It commands a price of about $500–600 per ton, as compared with $100–300 per ton for starch, $70–240 per ton for protein in the form of corn gluten feed or corn gluten meal, and about $320 per ton for ethanol. However, corn oil is produced by separation of the germ from the rest of the corn kernel by wet- or dry-degermination milling, followed by processing of the germ to recover the oil. The dry-grind process for producing ethanol does not aim to recover the oil at all, letting this valuable product pass through to the distiller's dried grains (DDG), which are sold as animal feed at a low price of $70–150/ton. Should a low-cost and simple addition to the process allow for the recovery of the oil, the producers could return more than half the value of corn that they currently receive from ethanol and DDG alone.

*To whom correspondence should be addressed at USDA, ARS, ERRC, 600 E. Mermaid Ln., Wyndmoor, PA, 19038.
E-mail: jkwiatkowski@arserrc.gov

A considerable amount of energy is expended in current oil-refining processes, with each step removing only one or two undesirable components. Energy is also consumed in the form of electricity, natural gas, and fuel oils to heat and cool the oil between processing steps. Membranes have been used successfully to separate the product and solvent streams using very little energy, and they are a low-cost manufacturing technology when compared with traditional unit operations. Membranes also allow for lower-temperature processing, preventing thermal damage to the products. With a slight alteration of process streams, the extraction and separation of oil may be achieved within the dry-grind process.

A major factor in the implementation of this process is the availability of nanofiltration membranes that perform well in ethanol. Work has been done previously to refine glyceride oils with membranes, including the separation of phospholipids in hexane (1). Few polymeric membranes are stable in hexane, and using a more polar solvent such as ethanol does not increase the choice of membranes available. Data in the literature on the transport and retention of nanofiltration membranes in organic solvents have been limited (2). Recently developed membranes are being used to perform separations in organic solvents.

The focus of this work was the development of a process for the production of corn oil that can be easily integrated into dry-grind plants and that uses in-house materials (ethanol and ground corn). The selection of membranes suitable for use in nonaqueous solvents and their subsequent characterization were the precursors to experiments testing the ability of the membranes to concentrate the extract feed, along with a comparison of their performance using a model solution of refined corn oil in ethanol.

EXPERIMENTAL PROCEDURES

Raw materials. Whole corn (yellow dent #2) with an average moisture content of 12% was obtained from a Midwest grain elevator (Anderson Grain Co., Champaign, IL) and used as-is with no screening. Ethanol (anhydrous, 200 proof containing 0.1–0.2% water as determined by Karl Fischer titration) was obtained from Aaper Alcohol and Chemical Company (Shelbyville, KY). Commercially refined corn oil was purchased from a local grocery store.

Membrane screening. The membranes listed in Table 1 were evaluated in initial trials. Screening experiments were carried

TABLE 1
Membranes Evaluated During Initial Trials[a]

Membrane	MWCO	Manufacturer	Polymer/type
TFC-S	60% NaCl rejection	Koch	Flat sheet/hydrophilic
TFC-SR1	88% NaCl rejection	Koch	Flat sheet/hydrophilic
TFC-SR2	95% NaCl rejection	Koch	Flat sheet/hydrophilic
SW-30	99.2% NaCl rejection	FilmTec	Flat sheet/hydrophilic
NF-45	200 Da	FilmTec	Flat sheet/hydrophilic
DK	300 Da	Osmonics-Desal	Flat sheet/hydrophilic
MPF-44	250 Da	Koch	Flat sheet/hydrophilic
MPF-60	400 Da	Koch	Flat sheet/hydrophobic
7450	"Nanofiltration"	Hydranautics	Flat sheet/(N/A)

[a]Koch: Koch Membrane Systems, Inc. (Wilmington, MA); FilmTec: Dow Chemical Co. (Midland, MI); Osmonics-Desal: Osmonics Inc. (Minnetonka, MN); Hydranautics: Hydranautics (Oceanside, CA). MWCO, molecular weight cutoff.

out in a Sepa-ST model membrane test cell (Osmonics Inc., Minnetonka, MN) with a magnetic stirrer and a nitrogen gas cylinder to provide pressure as the driving force for permeation. The cell is capable of withstanding pressures up to 6.9 MPa (1,000 psig) and holds a 5-cm diameter membrane disc (effective membrane area of 17.35 cm^2). Potable ethanol and deionized water microfiltered through a 0.2-mm filter were used in all experiments. Ethanol solutions were prepared as binary mixtures on a volume-by-volume (vol/vol%) basis as necessary. Flux was measured by the time required to collect a desired volume of permeate. The test cell was held in a water bath to simulate test conditions at alternate temperatures.

The membrane coupons were conditioned by the method of Shukla and Cheryan (3). The membrane coupon was first rinsed under running deionized water. The coupon was then soaked in solvent overnight and placed in the test cell for the trial. The cell was filled with 150–200 mL of solvent, and 10 min was allowed for the solvent to reach the temperature of the surrounding water bath (if necessary). The system was pressurized to the desired pressure (1.38, 2.76, or 4.14 MPa), and liquid was permeated until the flux had reached a steady value. The membrane was then removed and placed in a higher concentration of ethanol overnight. Conditioning was done in intervals of 10 and 20%, as well as at 1.38 and 2.76 MPa. The procedure was repeated for each membrane coupon until a concentration of 100% ethanol was reached.

Concentration studies. Extracts prepared previously using the process described in Kwiatkowski (4) were used to evaluate the performance of the DK, TFC-SR1, and TFC-SR2 membranes. The conditions for batch extraction were 30 min batch time, a temperature of 50°C, 100% (vol/vol) ethanol, and a 1:4 ratio of ground corn solids to solvent. After extraction, the slurry was filtered through Whatman #1 filter paper and used directly for studies with the membranes. Proximate analysis of the ethanol extract is as follows: total solids (g/L), 13.75; oil (g/L), 11.14; protein (g/L), 1.21; moisture (wt%), 1.49. The membranes were first conditioned up to 100% ethanol before processing with the extract solution. After testing, the membrane was washed with 100% ethanol and soaked overnight. The flux with pure ethanol was determined again and compared with the pure ethanol flux before exposure to the ethanol extract. Samples of feed, retentate, and permeate were taken during a run and analyzed for oil, total solids, and protein.

For the concentration studies, the corn oil in ethanol solutions were concentrated until the minimum volume capable of being stirred remained. A new corn oil in ethanol solution was prepared using the concentrated material remaining from the previous stage and was concentrated again. The ethanol extracts were concentrated to a volume concentration ratio (VCR) of 2. Initial experiments with the extracts were done with the TFC-SR1 and TFC-SR2 membranes at ambient temperature (22°C) and a pressure of 1.38 MPa. Subsequent experiments were done with all three membranes at 50°C and 1.38 MPa, followed by experiments at 50°C and 2.76 MPa. The flux throughout the experiment was monitored, and samples of the feed and retentate were analyzed for total solids. Samples of permeate were collected as well and analyzed for total solids and oil content by HPLC.

Proximate and sample analysis. The concentrations of pure corn oil in ethanol solutions were determined gravimetrically. Liquid samples were placed in a fume hood while the solvent evaporated, and the desolventized residue was dried in an oven at 103°C to remove the moisture. The weight of the residue after drying and the volume of the original liquid sample were used to determine the concentration. The particle size distribution of the milled corn was determined using a RO-tap shaker and U.S. standard sieves. Total solids of the extracts were determined by air-drying for at least 1 h and then by oven-drying at 103°C for 6 h or overnight. Nitrogen (N), for both whole corn and extracts, was determined by the combustion method (5). Protein is expressed as N × 6.25 (6). The oil content of whole corn was determined by the HPLC method developed in our laboratory (7) or by the Soxhlet method for solids, AOAC 920.39C (6).

Calculations. Flux (*J*) is defined as:

$$J\ (\text{LMH}) = \frac{\text{volume of permeate (L)}}{\text{membrane surface area } (\text{m}^2) \times \text{time (h)}} \quad [1]$$

where LMH is liters per meter squared per hour. Corn oil rejection (*R)* is defined as:

$$R\ (\%) = \left(1 - \frac{C_P}{C_R}\right) \times 100 \quad [2]$$

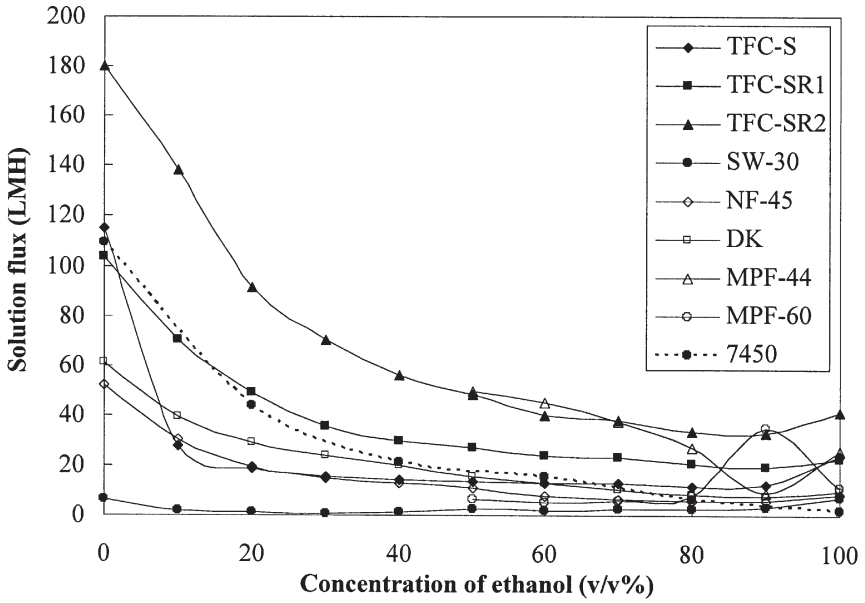

FIG. 1. Screening of all membranes from 0 to 100% ethanol/water. Membranes are characterized in Table 1. LMH, liters/m^2/h.

where C_P and C_R are the concentrations of corn oil in permeate and retentate in grams per liter, respectively. VCR is defined as:

$$\text{VCR} = \frac{\text{volume (feed)}}{\text{volume (retentate)}} \quad [3]$$

Pure solvent flux recovery is:

$$\text{recovery}\,(\%) = \frac{\text{pure solvent flux (after processing)}}{\text{pure solvent flux (before processing)}} \times 100 \quad [4]$$

All measurements were performed in duplicate. An independent estimate of error was determined for flux measurements with pure solvent. Error bars represent a 95% confidence interval.

RESULTS AND DISCUSSION

Membrane selection. Conditioning resulted in a flux decline with an increase in ethanol concentration for all membranes (Fig. 1). These results are all in agreement with previous conditioning studies with similar membranes done by Tsui and Cheryan (8). Of the membranes screened, three were chosen to be used in further studies: DK, TFC-SR1, and TFC-SR2. The membranes were conditioned at 50°C and 2.76 MPa for the concentration experiments with model corn oil solutions and ethanol extracts of corn.

Model corn oil system. An initial solution of 2.5 g/L corn oil in absolute ethanol was used as a starting point for the concentration studies with a model system of refined corn oil in ethanol. The feed to the each membrane was concentrated in two to three stages, reducing the volume as much as possible in the Sepa-ST cell for each stage. The concentration of oil with increasing VCR for each stage using the DK membrane is shown in Figures 2 and 3. The VCR achieved in the first stage was 6.25, producing a retentate that was concentrated to 14.4 g/L. For the second stage, a new 20 g/L corn oil in ethanol solution was prepared and concentrated under similar conditions and VCR to yield a retentate with 96 g/L corn oil in ethanol. A third and final solution of 88 g/L was prepared and concentrated to ~130 g/L corn oil in ethanol. The flux declined from 20 to 9.8 LMH over the three stages as the oil concentration increased (Fig. 3). Rejection of corn oil was >90% throughout, and it increased with the concentration of oil. The concentration of oil in the permeate fractions decreased with VCR for all three stages. On collection at 50°C, the retentate fractions from the Sepa-ST cell were opaque and cloudy. As the retentate cooled to room temperature (~22°C), a clear separation of oil and ethanol was seen.

The three-stage concentration with the TFC-SR1 membrane produced a retentate with 121 g/L corn oil in ethanol, whereas the concentration in the permeate was kept very low. The oil was concentrated to 5.5 g/L in the first stage and 34.6 g/L in the second stage (Fig. 4). The flux declined to 44 LMH at the end of stage three (Fig. 5), considerably higher than the flux achieved with the DK membrane. The rejection initially decreased and then increased to greater than 90% with an increasing concentration of oil. A gradual buildup of corn oil or interaction between the solute and membrane may have caused increased rejection.

Only two stages of the concentration experiment were completed for the TFC-SR2 membrane, as no rejection of corn oil was perceived during either stage. Although the flux was high compared with the other membranes (134 LMH at the end of stage 2), the membrane was unable to concentrate the model corn oil solutions at all. No linear trend could be seen between the flux and rejection vs. the log concentration of oil curves.

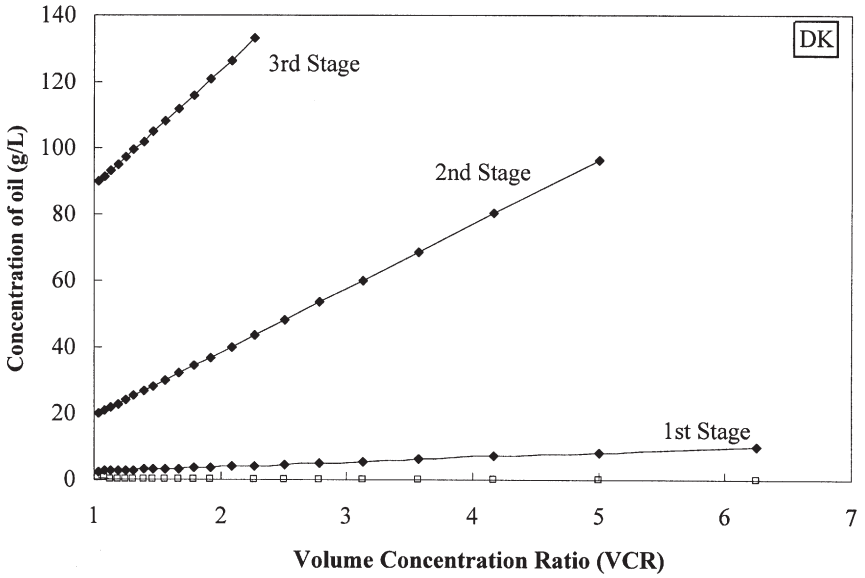

FIG. 2. Concentration of corn oil using the DK membrane (retentate, ◆; permeate, □). For membrane properties and manufacturer, see Table 1. LMH, liters/m^2/h.

Single-stage extract concentration. The flux declined with an increasing concentration of extract for the DK membrane at 50°C and 1.38 MPa. The extract flux was found to be much lower than with the pure solvent, but recovery of pure solvent flux after rinsing with ethanol was 91%. This indicates that little fouling of the membranes had occurred. Increasing the pressure to 2.76 MPa increased the extract flux from 6 LMH to a steady-state flux of 8 LMH. The pure solvent flux recovery after cleaning at this higher pressure was 95%.

The TFC-SR1 membrane gave similar results at ambient temperature and 1.38 MPa. The extract flux was very low compared with pure solvent flux for the TFC-SR1 (1–2 vs. 27 LMH). The recovery of pure solvent flux at ambient temperature was only 20%, clearly indicating fouling in the presence of extract solution. Operating the system at 50°C had a positive effect, bringing the flux to 28 LMH at 1.38 MPa and to 35.6 LMH at 2.76 MPa. The recovery of pure solvent flux was 89% at 1.38 MPa and 86% at 2.76 MPa.

The TFC-SR2 performed poorly at ambient temperature, achieving an extract flux of less than 1 LMH, and the pure

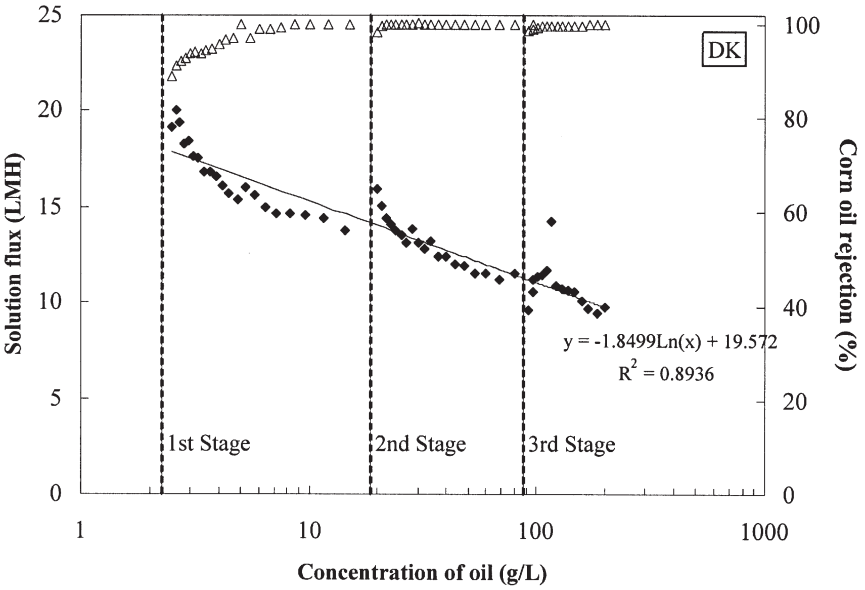

FIG. 3. Flux and rejection during concentration of corn oil using the DK membrane (flux, ◆; rejection, △). For membrane properties and manufacturer, see Table 1.

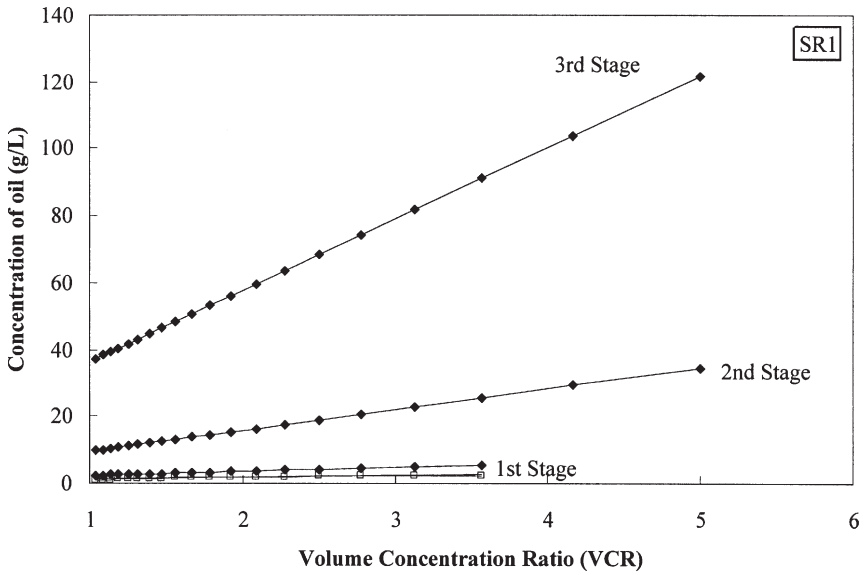

FIG. 4. Concentration of corn oil using the TFC-SR1 membrane (retentate, ◆; permeate, □). For membrane properties and manufacturer, see Table 1.

ethanol flux recovery after cleaning was only 11%. Increasing the temperature to 50°C dramatically increased the extract flux to 28.2 LMH, but the membrane still showed a significant indication of fouling, as the pure solvent flux recovery was only 50%.

The three membranes responded similarly, with an increase in extract flux in response to increasing pressure. The extract flux of the DK membrane was significantly less than that of the two TFC membranes, however. The rejection of oil by the DK membrane was slightly greater than that of the TFC-SR1 membrane, but both were above 98%. The TFC-SR2 had a much higher rejection than with the model corn oil system, 89 vs. 10%, respectively. This was surprising considering how low the rejection of oil was when using the model solution of corn oil in ethanol.

Multistage extract concentration. The multistage experiments were completed by collecting the retentate from three runs of the single-stage experiment to make up enough concentrated extract for the second stage. The retentate from the single-stage runs was pooled and used as the feed for a second stage. The reproducibility of the flux data from experiments with the single-stage extract was quite good. Generally, the

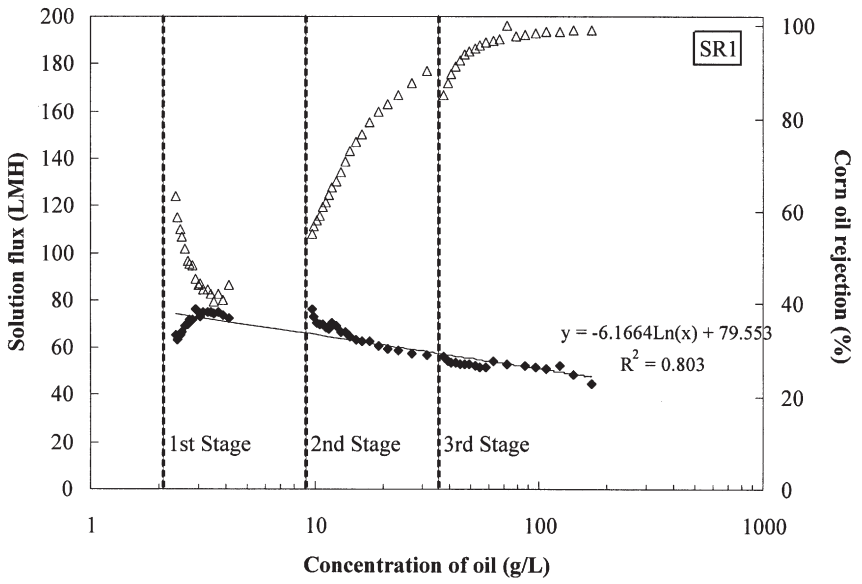

FIG. 5. Flux and rejection during concentration of corn oil using the TFC-SR1 membrane (flux, ◆; rejection, △). For membrane properties and manufacturer, see Table 1. LMH, liters/m^2/h.

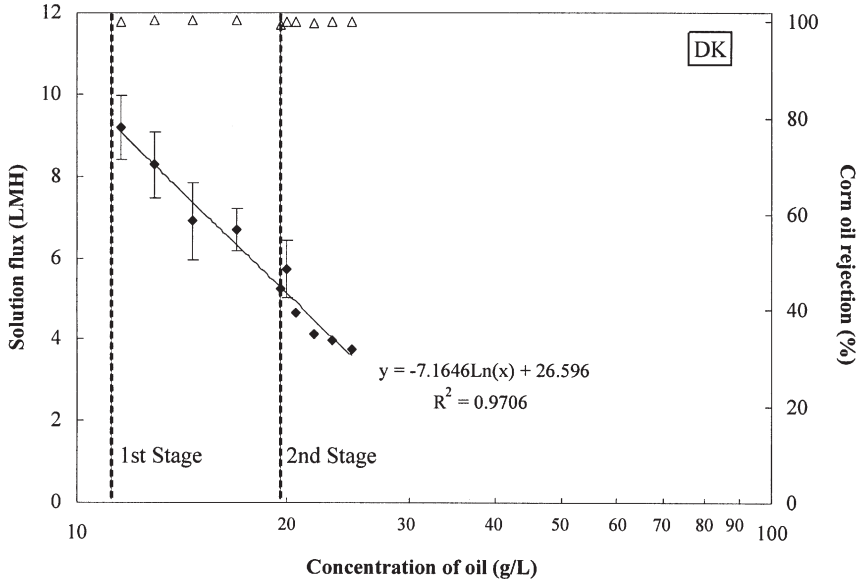

FIG. 6. Flux and rejection during concentration of ethanol extract using the DK membrane (flux, ◆; rejection, △). Error bars indicate the 95% confidence interval of the measurements. For membrane properties and manufacturer, see Table 1. LMH, liters/m^2/h.

second-stage flux declined to half that of the first stage. An increase in the VCR resulted in concentration of the feed similar to that seen with the model corn oil system.

For the DK membrane, pooled extract from the first stage was concentrated from 11.6 to 20.0 g/L solids in the first stage, a VCR of nearly 2 (Fig. 6). From 20.0 g/L, it was concentrated to 24.8 g/L with the second stage. The data were nearly linear on a semilog plot, which follows a classic film theory prediction of transport. The rejection was 100% for all multistage concentration experiments using the DK membrane. The DK membrane also recovered all 100% of its pure solvent flux with a simple rinsing and soaking with ethanol after completion of the experiments.

The TFC-SR1 membrane had a much higher extract flux than the DK membrane for both stages (Fig. 7). A similar 50% decrease was seen in second-stage flux from the first stage,

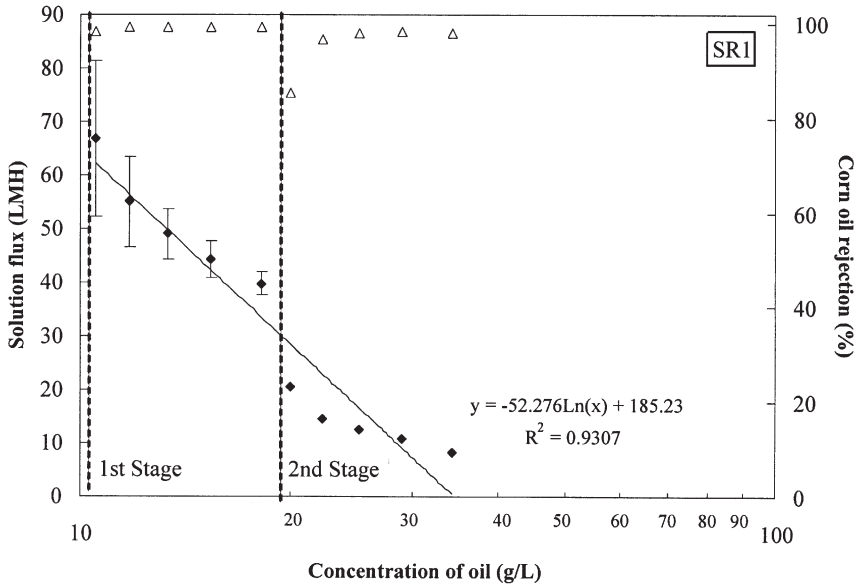

FIG. 7. Flux and rejection during concentration of ethanol extract using the TFC-SR1 membrane (flux, ◆; rejection, △). Error bars indicate the 95% confidence interval of the measurements. For membrane properties and manufacturer, see Table 1. LMH, liters/m^2/h.

however. The membrane was able to concentrate the oil in the retentate from 10.5 to 18.0 g/L in the first stage. The extract was concentrated further from 20.0 to 34.3 g/L in the second stage. The response of flux with the log concentration of oil was approximately linear. The rejection of solids and oil was greater than 90% with an increasing concentration of oil. However, the TFC-SR1 membrane recovered only 68% of the pure solvent flux after cleaning.

The TFC-SR2 membrane was surprisingly successful in concentrating the ethanol extract, although it did not perform as well as the DK and TFC-SR1. The flux with VCR was comparable to the values obtained for the TFC-SR1 membrane, and the reproducibility was good as well. Beginning at 10.6 g/L of oil, the first stage extract was concentrated to 18.0 g/L. In the second stage, the extract was concentrated from 19.9 to 32.9 g/L. The rejection of solids reached 97%, but then dropped to 89.6% as the experiment progressed into the second stage, indicating that material was leaking through. The noticeably yellow color of the permeate made it evident that material was passing through the membrane, whereas permeates from the DK and TFC-SR1 membranes were colorless. The TFC-SR2 also showed significant evidence of membrane fouling, with a pure solvent flux recovery after cleaning of only 41%. Although it proved able to concentrate the extract solution, its unpredictable behavior makes the TFC-SR2 a poor choice.

ACKNOWLEDGMENTS

This research was supported in part by the Illinois Department of Commerce and Community Affairs, the USDA National Research Initiative Competitive Grants Program, the Illinois Corn Marketing Board, and the American Oil Chemists' Society Foundation. We would like to thank Kevin Hicks for a careful review of the manuscript.

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[Received November 30, 2005; accepted February 8, 2005]