Deacidifying Rice Bran Oil by Solvent Extraction and Membrane Technology

V. Kale[1], S.P.R. Katikaneni, and M. Cheryan*

University of Illinois, Agricultural Bioprocess Laboratory, Urbana, Illinois 61801

ABSTRACT: Crude rice bran oil containing 16.5% free fatty acids (FFA) was deacidified by extracting with methanol. At the optimal ratio of 1.8:1 methanol/oil by weight, the concentration of FFA in the crude rice bran oil was reduced to 3.7%. A second extraction at 1:1 ratio reduced FFA in the oil to 0.33%. The FFA in the methanol extract was recovered by nanofiltration using commercial membranes. The DS-5 membrane from Osmonics/Desal and the BW-30 membrane from Dow/FilmTec gave average FFA rejection of 93–96% and an average flux of 41 L/m^2·h (LMH) to concentrate the FFA from 4.69% to 20%. The permeate, containing 0.4–0.7% FFA, can be nanofiltered again to recover more FFA with flux of 67–75 LMH. Design estimates indicate a two-stage membrane system can recover 97.8% of the FFA and can result in a final retentate stream with 20% FFA or more and a permeate stream with negligible FFA (0.13%) that can be recycled for FFA extraction. The capital cost of the membrane plant would be about $48/kg oil processed/h and annual operating cost would be about $15/ton FFA recovered. The process has several advantages in that it does not require alkali for neutralization, no soapstock nor wastewater is produced, and effluent discharges are minimized.

Paper no. J8957 in *JAOCS 76*, 723–727 (June 1999).

KEY WORDS: Deacidification, extraction, free fatty acids, membrane technology, methanol extraction, nanofiltration, rice bran oil, refining.

The main steps in conventional refining of vegetable oil are degumming (optional), deacidifying, bleaching, and deodorizing. The chemical and physical deacidification processes used to remove free fatty acids (FFA) have some limitations (1,2): large quantities of water and chemicals are used, large amounts of wastewater are generated, they may be energy intensive, and there are losses of neutral oil. Membrane technology may be a way to overcome many of these problems (2–4) and can provide an opportunity to develop alternative environment-friendly processes for refining vegetable oils. One of our earlier studies (5) focused on the use of nanofiltration (NF) membranes for simultaneously desolventizing and removing FFA from soybean oil, which resulted in partial (50%) reduction in FFA concentration. A better process may be to combine NF with solvent extraction (6). The FFA is first extracted with methanol. Following phase separation, the methanol phase containing the FFA is nanofiltered to result in a FFA concentrate stream and a permeate stream containing the methanol which is recycled to the extractor.

Most work on membrane refining to date has focused on soybean oil and usually model oils obtained by adding FFA to refined oil (6,7). The commercial crude rice bran oil used in this study had much higher FFA (15–30% of the oil) and contained waxes, colored compounds, and phospholipids. The gums in rice bran oil can be removed by ultrafiltration (8). The present paper reports the use of solvent extraction and membrane processing to deacidify crude rice bran oil.

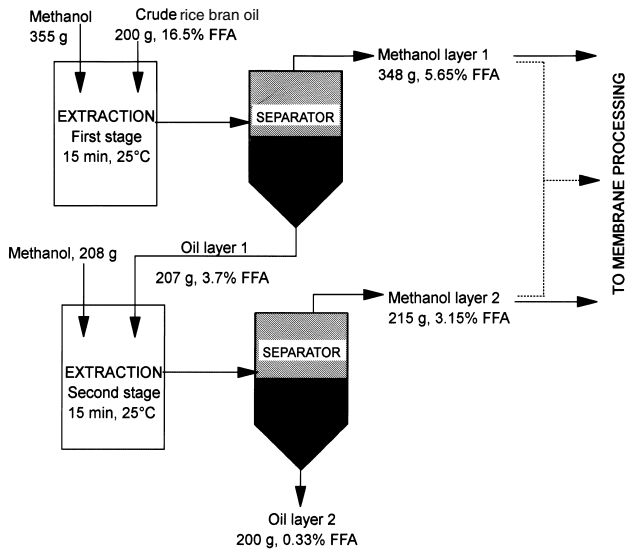
EXPERIMENTAL PROCEDURES

Extraction of FFA from crude rice bran oil. Crude rice bran oil supplied by Ramchandran Oil Industries, Kattedan, Hyderabad, India, contained 1.7% phospholipids, 16.5% FFA, and 4% waxes. Preliminary experiments established the optimal ratio of 1.8 g of methanol per g crude oil to maximize the amount of FFA extracted with minimum dilution of FFA in the extractant. Crude rice bran oil was mixed with the methanol in a separatory funnel. After 30 min of vigorous shaking, the oil–methanol mixture was allowed to settle. Complete phase separation typically took 30 min. The oil phase at the bottom of the funnel was removed and used for a second solvent extraction step, if necessary. The methanol phase from each extraction stage was collected and subjected to NF. The extraction temperature was 24°C. The complete flow sheet and material balance for the FFA extraction with methanol in two stages is shown in Scheme 1.

Membrane filtration. NF experiments were conducted in a stainless-steel membrane cell (Osmonics Inc., Minnetonka, MN) having a diameter of 8 cm and height of 25 cm. The cell could withstand pressures of 6.9 MPa and accommodate 300 mL of feed. A sintered stainless-steel circular disc supported a flat membrane sheet with an effective area of 14.5 cm^2. Pressure was applied from a nitrogen gas cylinder. A magnetic stir bar just above the membrane minimized concentration polarization effects. Permeate was removed from the downstream side of the membrane through 1/8″ stainless-steel tubing. Retentate was removed from the cell through a similar tube with a valve on top of the cell. Further details of the cell have been given in an earlier publication (6).

[1]Present address: Indian Institute of Chemical Technology, Hyderabad, 500007, India.

*To whom correspondence should be addressed at University of Illinois at Urbana-Champaign, Agricultural Bioprocess Laboratory, 1302 W. Pennsylvania Ave., Urbana, IL 61801. E-mail: mcheryan@uiuc.edu



SCHEME 1

Membranes from several manufacturers were initially screened for stability to methanol, flux of methanol, and rejection of fatty acids, as described by Raman *et al.* (6). Two promising membranes were selected for further study: DS-5 (Osmonics/Desal, Minnetonka, MN) and BW-30 (FilmTec, Minneapolis, MN).

The FFA/methanol extract was placed in the membrane cell, which was then placed in a water bath to control temperature. After pressurizing to the desired pressure, samples of permeate and retentate were taken for FFA analysis. Flux was measured simultaneously by timing the flow rate of permeate and is expressed in L/m^2 · h (LMH):

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

Flux is one of two important parameters in membrane technology (9) and should be as high as possible to minimize capital cost. The other important parameter is rejection, which describes the separation capability of a membrane. It has a value from 0 to 100% and is defined as (9)

$$\text{rejection (\%)} = (1 - C_P/C_R) \times 100 \quad [2]$$

where C_P and C_R are concentrations of the component in the permeate and retentate, respectively. In this application, the ideal membrane would have zero rejection for methanol and 100% rejection of FFA.

Volume concentration ratio (VCR) characterizes the extent of membrane processing (9). It also affects capital and operating costs,

$$\text{VCR} = \frac{\text{initial volume of feed}}{\text{volume of retentate}} \quad [3]$$

Analytical methods. FFA was estimated by acid value (AV) by titration with an alkali. The titration end point was determined using phenolphthalein as indicator. The AV was expressed as mg KOH per g of sample. FFA was expressed as percent oleic acid calculated according to American Oil Chemists' Society Method Cd 3d-63 (10).

RESULTS AND DISCUSSION

Extraction. Preliminary experiments indicated that a methanol/oil ratio of 1.8:1 (by weight) was optimal for the first-stage extraction. After extraction, the FFA in the oil decreased from 16.5 to 3.7% while the upper methanol phase contained 5.65% FFA. The oil phase was extracted again with fresh methanol, but this time the methanol ratio was reduced to 1:1, since the amount of FFA present in the oil had been reduced significantly in the first-stage extraction and to minimize the cost of subsequent membrane processing. FFA decreased to 0.33% in the oil phase after the second extraction. The methanol phase from this second extraction contained 3.15% FFA. The methanol phases from the two extraction stages were either nanofiltered separately or were combined and then nanofiltered.

NF. Preliminary NF experiments with the methanol extracts were done at various pressures (0.7–4.2 MPa) and temperatures (25–50°C) to establish the range of possible operating conditions. Figure 1 shows the performances of the BW-30 and DS-5 membranes in terms of VCR. As expected for a high-rejection membrane, the FFA concentration in the retentate increased almost linearly from 50.2 g/L at VCR 1 to 190.7 g/L at VCR 4.4. The FFA concentration in the permeate was much lower, averaging 4–7 g/L. This resulted in average FFA rejection of 91–96%, with rejection increasing with VCR. At VCR 4.4, about 78% of the original volume of methanol was recovered as permeate, which could be recycled to the extraction stages or sent for additional NF, if necessary.

Figure 2 shows the effect of FFA concentration on flux. Increasing FFA concentration resulted in decreased flux, owing to decreased driving force for permeation. The data were correlated as follows:

$$\text{flux (LMH)} = 142 - 21.9 \ln (C_{\text{FFA}}) \quad [4]$$

where C_{FFA} is the concentration of FFA expressed as g/L of methanol extract. The correlation coefficient (r^2) was 0.86, standard error of the y estimate was 8.55, and the standard error of the coefficient was 2.26. When flux data were extrapolated to zero flux, they indicated a maximum of about 655 g/L FFA could be obtained under these operating conditions. These data are similar to those reported for soybean oil with added oleic acid (6) except that the flux was one-half of what we found. This could be because our experiments were conducted at higher temperature (50 vs. 25°C) and higher pressure (2.75 vs. 1.73 MPa). Depending on the mechanism of transport (e.g., mass-transfer-limited vs. osmotic-pressure-limited), higher pressure could result in higher flux and higher FFA concentration (9,11).

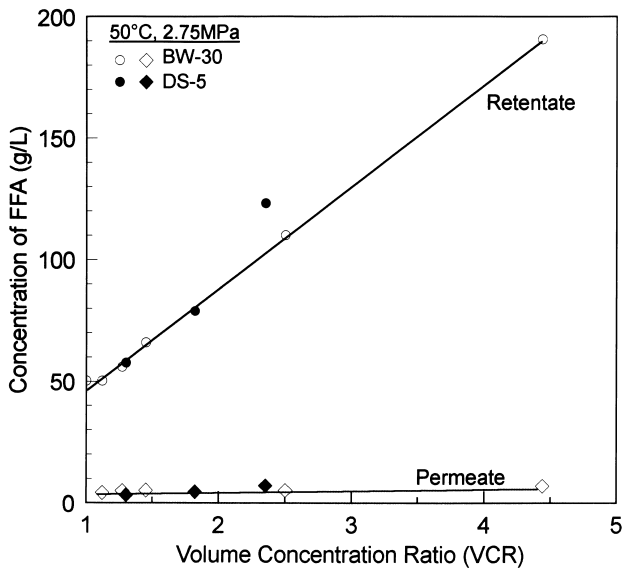


FIG. 1. Nanofiltration of methanol extracts of crude rice bran oil: effect on free fatty acid (FFA) concentration in retentate and permeate. Data obtained with methanol extracts from first stage extraction. Open points are data with the BW-30 membrane (FilmTec, Minneapolis, MN), solid points with DS-5 membrane (Osmonics/DeSal, Minnetonka, MN).

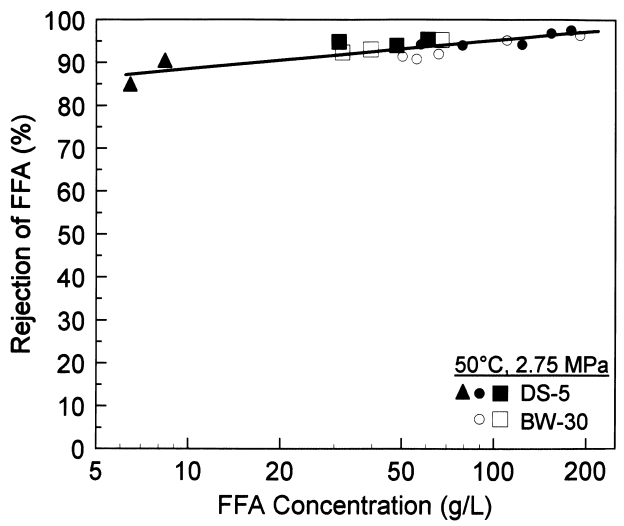


FIG. 3. Rejection of FFA in methanol extracts of crude rice bran oil. For abbreviation and manufacturers see Figures 1 and 2. Line drawn according to Equation 5.

Figure 3 shows the effect of FFA concentration on rejection by the two membranes. Rejection increased with FFA concentration, a phenomenon observed with many reverse osmosis and NF applications (11,12). Rejection data were expressed as follows:

$$\text{rejection (\%)} = 80.9 + 3.1 \ln (C_{FFA}) \quad [5]$$

The correlation coefficient (r^2) was 0.76, the standard error of the y estimate was 1.56, and the standard error of the coefficient was 0.44.

Since the membranes did not reject 100% of the FFA in the methanol extracts, a small quantity escaped into the permeate. A multistage process could be used to increase the recovery of FFA; the permeate from the first-stage NF could be fed into another NF system to recover more of the FFA, and so on with multiple stages.

System design. A preliminary design of a system to recover FFA from methanol extracts by multistage NF is shown in Scheme 2 for a plant capacity of 10,000 kg/h of crude rice bran oil. The temperature was assumed to be 50°C and transmembrane pressure was 2.75 MPa (400 psi). The design goal was the production of a retentate stream containing 20% FFA that would go to the methanol evaporator, and a permeate stream with a low level of FFA that could be directly recycled to the extractor (Table 1).

The extraction was done in two stages with a weight ratio of 1.8:1 methanol-to-oil in the first stage and 1:1 ratio in the second stage. The total weight of methanol used was 2.8 kg/kg oil. Thus, the feed to the membrane system would ideally be 28,000 kg/h containing 4.69% (w/w) FFA. The first stage of the membrane system concentrates the FFA from 4.69 to 20% with a VCR of 4.6. From Equation 5, the average FFA rejection was 95% in the first stage. The flow rate of permeate from the first stage was 21,913 kg/h (24,690.8 L/h) with 0.44% FFA, which was processed in the second membrane stage. The second stage had an average FFA rejection of 91%. A VCR of

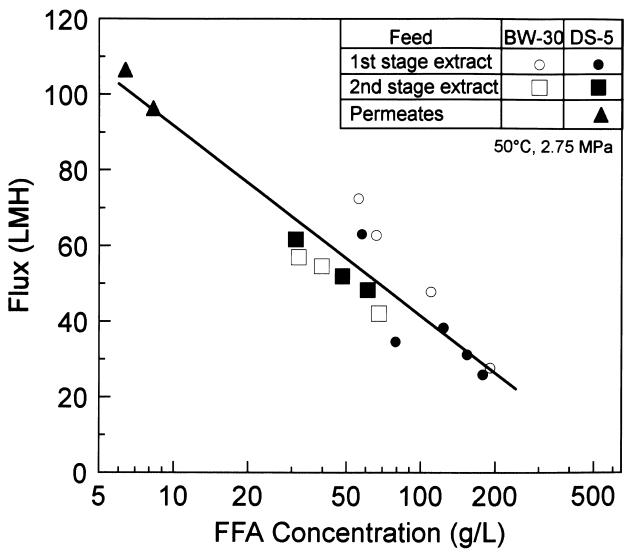
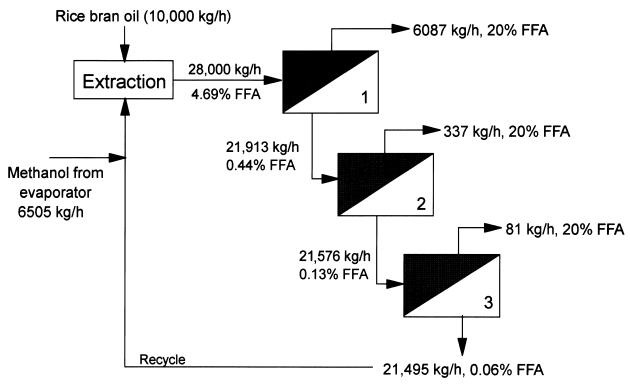


FIG. 2. Nanofiltration of methanol extracts of crude rice bran oil: effect of FFA concentration in the feed (or retentate) on flux. Data obtained with methanol extracts from a one-stage extraction (circles) or from the second stage of extraction (squares) as shown in Scheme 1. The triangles represent data with permeates from the first stage of nanofiltration. Open points are data with the BW-30 membrane; solid points with DS-5 membrane. Line drawn according to Equation 4. Abbreviation: LMH, $L/m^2 \cdot h$; for other abbreviation and manufacturers see Figure 1.

TABLE 1
Process Design for Multistage Membrane System for Recovery of FFA from Methanol Extracts of Rice Bran Oil[a]

	1st Stage	2nd Stage	3rd Stage
Feed flow rate (kg/h)	28,000	21,900	21,600
FFA in feed (% w/w)	4.69	0.44	0.13
Rejection (%)	95	91	90
Volume concentration ratio	4.6	65	266
FFA in retentate (%)	20	20	20
FFA in permeate (%)	0.44	0.13	0.06
Recovery of FFA in each stage's retentate (kg/h)	1,217	67.4	16.3
Value of FFA in each stage's retentate ($/yr[b])	5,621,000	311,000	75,000
Average flux (L/m^2 · h)	41	67	75
Permeate flow (L/h[c])	24,690	24,310	24,220
Membrane area in each stage (m^2)	602	363	323

[a]FFA, free fatty acid.
[b]FFA price = $550/ton.
[c]Density of methanol = 0.8875 kg/L.



SCHEME 2

65 in the second stage resulted in a second-stage retentate with 20% FFA and 0.13% FFA in the permeate. The second-stage permeate may be recycled to the extractor or nanofiltered again as shown in Scheme 2. The third stage would have to be operated to a VCR of 266, which results in an average FFA rejection of 90%, a retentate with 20% FFA, and a permeate with 0.06% FFA. It should be remembered that while the permeate from the third stage goes directly back to the extractor, the retentates from each stage go to evaporation. The evaporated methanol is returned to the extractor.

The membrane plant has been designed according to methods suggested by Cheryan (9). Since organic solvents are being processed, the membrane plant requires more rigorous construction than a water-based membrane plant. Thus, the plant cost has been increased by 50% to $500/m^2. Average flux was calculated from Equation 4 and used to obtain the required membrane area in each stage. As shown in Table 2, the capital cost of a one-stage membrane plant is about $301,000, equivalent to about $30/kg/h of oil processed. A three-stage plant will cost $64/kg/h of crude oil. The annual operating cost was based on depreciation, membrane replacement, cleaning, labor, and maintenance as discussed by Cheryan (9). Operating cost varies from $9.8 to $19.7 per ton of FFA recovered, depending on the number of stages.

Although FFA recovery increases from 93% with one stage to 99% with three stages (Table 2), the amount of methanol recycled from the membrane system decreases slightly, resulting in slightly more methanol to be evaporated (4870 kg/h with one stage vs. 5205 kg/h with three stages). In addition, the capital and annual operating cost of the membrane plant increases with the number of stages. However, the value of the FFA recovered compensates for the additional stages. The FFA recovered in a one-stage plant is 10,220 tons/yr, worth over $5.62 million (assuming a FFA value of $550/ton). In terms of value gained, since the annual operating cost is about $100,000, the membrane plant is worth $56 per $ of operating cost. Adding a second stage results in an additional $311,000 of FFA recovered per year for an additional operating cost of $61,000, which gives a value gain of $5 per $ operating cost for the second stage alone. A third stage has a value gain of about $1.4/per $ operating cost. As shown in Table 2, although the net value gain decreases with

TABLE 2
Recoveries and Cost Estimates of Membrane System for Refining Crude Rice Bran Oil[a]

	One-stage plant	Two-stage plant	Three-stage plant
Total recovery of FFA (%)	93	98	99
Net methanol recycle (%)	78	77	77
Capital cost ($)	301,000	483,000	644,000
Annual operating cost ($/yr)	100,000	161,000	215,000
Annual operating cost ($/ton FFA recovered)	9.8	14.9	19.7
Value gain ($ of FFA/$ operating cost)	56.0	36.9	28

[a]For abbreviation and assumptions, see Table 1.

more stages, a three-stage plant is still an attractive value gain of $28/per $ of operating cost.

Although the data were obtained in a small laboratory-scale test cell, they provide a basis for evaluating the feasibility of the concept and estimating economic advantage. Pilot testing will be necessary to obtain design data relating to membrane life, cleaning cycles, and purity of the product streams.

ACKNOWLEDGMENTS

The authors thank the Council of Scientific and Industrial Research (CSIR), India, for financial assistance to V. Kale to conduct the research at the University of Illinois. Contributions from Osmonics/Desal, Dow/FilmTec, and Koch Membrane Systems are appreciated. Additional support was provided by the Illinois Agricultural Experiment Station.

REFERENCES

1. Carr, R.A., Degumming and Refining Practices in the U.S., *J. Am. Oil Chem. Soc. 53*:347–352 (1976).
2. Raman, L.P., N. Rajagopalan, and M. Cheryan, Membrane Technology, *Fats Oils Int. (UK) 10*:28–34 (1994).
3. Cheryan, M., L.P. Raman, and N. Rajagopalan, Vegetable Oil Refining by Membrane Technology, in *Proceedings of the Sixth International Conference on Engineering and Food*, edited by T. Yano, R. Matsuno, and K. Nakamura, Blackie Academic Press, Tokyo, 1994, pp. 677–680.
4. Koseoglu, S.S., J.T. Lawhon, and E.W. Lusas, Membrane Processing of Crude Vegetable Oils: Pilot Plant Scale Removal of Solvent from Oil Miscella, *J. Am. Oil Chem. Soc. 67*:315–322 (1990).
5. Raman, L.P., N. Rajagopalan, and M. Cheryan, Solvent Recovery and Partial Deacidification of Vegetable Oils by Membrane Technology, *Fette/Lipid 98*:10–14 (1996).
6. Raman, L.P., M. Cheryan, and N. Rajagopalan, Deacidification of Soybean Oil by Membrane Technology, *J. Am. Oil Chem. Soc. 73*:219–224 (1996).
7. Krishna Kumar, N.S., and D.N. Bhowmick, Separation of Fatty Acids/Triglycerols by Membranes, *Ibid. 73*:399–401 (1996).
8. Lin, L., K.C. Rhee, and S.S. Koseoglu, Bench-Scale Membrane Degumming of Crude Vegetable Oil: Process Optimization, *J. Membrane Sci. 134*:101–108 (1997).
9. Cheryan, M., *Ultrafiltration and Microfiltration Handbook*, Technomic Publishing Co., Inc., Lancaster, 1998.
10. American Oil Chemists' Society, *Official and Tentative Methods,* American Oil Chemists' Society, Champaign, 3rd edn., 1985.
11. Cheryan, M., Concentration of Liquid Foods by Reverse Osmosis, in *Handbook of Food Engineering,* edited by D.B. Lund and D.R. Heldman, Marcel Dekker, New York, 1992, pp. 393–436.
12. Raman, L.P., M. Cheryan, and N. Rajagopalan, Consider Nanofiltration for Membrane Separations, *Chem. Eng. Prog. 90*:68–74 (1994).

[Received July 23, 1998; accepted February 24, 1999]