Carotenoids from Red Palm Methyl Esters by Nanofiltration

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ABSTRACT: Palm oil contains high concentrations of carotenoids and tocopherols that can be recovered by first converting them to methyl esters and then applying membrane technology to separate the carotenoids from the methyl esters. Several solvent-stable nanofiltration membranes were investigated for this application. Flux with a model red palm methyl ester solution ranged from 0.5 to 10 $Lm^{-2}h^{-1}$, and rejection of β-carotene was 60–80% at a transmembrane pressure of 2.76 MPa and 40°C. A multistage membrane process was designed for continuous production of palm carotene concentrate and decolorized methyl esters. With a feed rate of 10 tons per hour of red palm methyl esters containing 0.5 gL^{-1} β-carotene, the process could produce 3611 $L{\cdot}h^{-1}$ of carotene concentrate containing 1.19 gL^{-1} carotene and 7500 Lh^{-1} of decolorized methyl esters containing less than 0.1 gL^{-1} β-carotene. The economics of this process is promising.

Paper no. J11133 in *JAOCS 83*, 365–370 (April 2006).

KEY WORDS: Carotene, membrane, methyl esters, nanofiltration, palm oil.

One of the unique characteristics of palm oil is its high content of carotenoids and tocopherols. Carotenoids, which impart the distinctive orange-red color to palm oil, together with tocopherols, contribute to the stability and nutritional value of palm oil. Typically, crude palm oil contains 500–700 ppm of carotenoids (0.5–0.7 gL^{-1}) and 800 ppm of tocopherols. The major carotenoids of palm oil are α- and β-carotenes, which constitute more than 80% of the total carotenoids in palm oil (1–5).

The primary uses of carotenes are as food colorants and pharmaceuticals. The benefits of carotenes to human health are well documented. Carotenes can function as a source of provitamin A or as antioxidants that may prevent the development of diseases such as rough skin, weakness of the mucous membranes, and cancer. Currently, the main commercial method of producing carotenes is by chemical synthesis (1). Carotenes extracted from natural sources such as palm oil could have a higher market value, especially for nutraceuticals and cosmetics.

The extraction and recovery of carotenes from palm oil would add significant value to the palm oil industry. Unfortunately, during conventional palm oil refining, these carotenoids are removed to give the light-colored oil required by consumers. Several processes have been developed to recover carotenoids from palm oil (2–4): One was developed by the Lion Corporation of Japan and uses transesterification followed by solvent extraction. The other process uses transesterification followed by molecular distillation to separate carotene from the red palm methyl esters (RPME) (5). Although these processes can produce concentrated palm carotenes, they require large amounts of energy for evaporation because of the high latent heat of the esters.

There is growing interest in the application of membrane technology for oil processing (6–12). The main reasons for using membranes are to separate components according to molecular size without a change of phase of the solvent, to minimize thermal damage, to recycle the solvents, for lower emissions, for lower energy consumption, to decrease oil losses, and to reduce bleaching earth requirements. Specific applications of membranes in vegetable oil processing include degumming, desolventizing, deacidification, decoloration, and dewaxing (5,6). This paper reports on a novel approach for recovering vitamins and pigments from vegetable oil using membrane technology, specifically, the recovery of carotenoids from red palm oil. Red palm oil is first transesterified to produce RPME. Since the carotenes have an average M.W. of approximately 536, they fall into the pore size range of nanofiltration (NF) membranes (6). The RPME are then nanofiltered to separate the carotenes from the methyl esters. This concept was evaluated using model systems of β-carotene added to palm oil that had been transesterified according to methods developed in our laboratory (13,14).

MATERIALS AND METHODS

Materials. Refined, bleached, and deodorized (RBD) palm oil was obtained from ADM (Decatur, IL). *Trans* β-carotene was purchased from Sigma Chemical Co. (St. Louis, MO). Flat sheet membranes were obtained from GE-Osmonics Inc. (Minnetonka, MN) and Koch Membrane Systems Inc. (Wilmington, MA). Palm methyl esters were prepared by transesterification of RBD palm oil as described earlier (13,14). This product is referred to in this paper as pure palm methyl esters. To simulate RPME, β-carotene was added to the palm methyl ester solution at the desired concentration, and is referred to in this paper as RPME.

Membrane system. A stainless-steel stirred cell (SEPA ST; GE-Osmonics Inc.) was used, as described by Raman *et al*. (11,12). Flat-sheet membranes with a diameter of 5 cm (effective membrane area of 14.5 cm^2) were used. Flux and rejection are important performance parameters of a membrane process, in addition to stability and lifetime of the membrane (6). Flux (J) is expressed as liters of permeate per square meter of membrane

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TABLE 1
Properties of the Membranes

Membrane	DS7	MPF60	MPF44
Hydrophilicity	Hydrophobic	Hydrophobic	Hydrophilic
M.W. cutoff	Not rated	400	250
pH range	1–12	2–10	2–10
Maximum temperature (°C)	100	40	40
Maximum pressure (MPa)	4.2	2.7	2.7
Manufacturer	GE-Osmonics (Minnetonka, MN)	Koch (Wilmington, MA)	Koch (Wilmington, MA)

area per hour (L m^{-2} h^{-1}). Rejection (R) is defined as $[1 - C_P/C_R]$ where C_P is the concentration of solute in the permeate and C_R is its concentration in the retentate. Experiments were done up to a volume concentration ratio (VCR) of 10, where VCR is written as X and defined in a batch process as the ratio of initial feed volume to retentate volume. In a continuous process, VCR is expressed as the ratio of feed flow rate to retentate flow rate.

After each experiment, the membrane was washed with hexane several times until the original hexane flux was recovered.

Membrane screening. Preliminary results and literature studies showed that only a few membranes were able to separate low-M.W. hydrophobic components. Among those membranes were DS7 (GE-Osmonics Inc.), MPF44, and MPF60 (Koch Membrane Systems Inc.). The known properties of the membranes are shown in Table 1. The membranes were studied with model systems for their ability to separate carotenes from methyl esters. The best one was used for further studies.

Analysis. Total carotenes were analyzed using a spectrophotometric method at 446 nm (3,15). Samples (about 0.1 g) of feed, permeate, or retentate were diluted with spectrophotometric-grade hexane to 25 mL, and the absorbance was measured using an HP Model 3854 spectrophotometer. All analytical tests were replicated at least twice and averages are reported.

RESULTS AND DISCUSSION

Membrane selection. Initial screening was done at 40°C and 2.76 MPa (400 psi) using RPME containing about 500 g L^{-1} β-carotene as the feed (this is the typical carotene concentration of crude palm oil produced in Southeast Asia). Figure 1 shows that MPF44 had the highest rejection of β-carotene (81.6%), followed by MPF60 (78.2%) and DS7 (65.3%). However, the flux was in the reverse order. The DS7 had the highest flux (10 L m^{-2} h^{-1}), followed by the MPF60 (1.7 L m^{-2} h^{-1}) and the MPF44 (0.17 L m^{-2} h^{-1}). The manufacturer classifies the MPF44 membrane as hydrophilic and is designed for polar solvents such as ethanol, methanol, or isopropanol. Less polar solvents, such as methyl esters, would result in lower flux. In addition, the nominal M.W. cutoff (MWCO) of the membrane is 250, which is close to the M.W. of the methyl esters (approx. 300). The MWCO of the MPF60 membrane is slightly higher than the M.W. of methyl esters, which resulted in a much higher flux but a slightly lower rejection. Although the rejection of DS7 was lowest (63.5%), it had the highest flux (10 L m^{-2} h^{-1}). Preliminary calculations showed that this combination of high flux and moderate rejection was more advantageous than high rejection and very low flux. Therefore, this membrane was selected for subsequent experiments.

Flux of solvents. For hydrophilic membranes, water is used to study initial membrane characteristics and for evaluating cleaning efficiency (6). However, the palm methyl ester–carotene system is hydrophobic; thus, methyl esters and hexane were used for testing the flux. Figure 2 shows the effects of temperature and pressure on hexane flux, and Figure 3 shows the flux of pure palm methyl esters with the DS7 membrane. The flux of methyl esters was approximately 6 times lower than hexane under similar conditions. This is not unexpected, since the M.W. of esters is approximately 6 times greater than hexane.

According to the Hagen–Poiseuille model of membrane transport (6), pure solvent flux is proportional to the applied pressure and inversely related to viscosity. Viscosity decreases at higher temperatures; thus, increasing the temperature will increase the flux. This is shown in Table 2, which lists the permeability values of hexane and methyl esters with the DS7 membrane as a function of temperature. Hexane permeability varies between 27 and 37 L m^{-2} h^{-1}/MPa. In contrast, Raman *et al*. (12) reported the hexane permeability of MPF-50 membrane as 15 L m^{-2} h^{-1}/MPa at 24°C. The relative permeability of methyl esters vs. hexane increased at higher temperatures.

Effect of temperature with RPME. Temperature affects flux and rejection by altering the viscosity and diffusivity (16). Figure 4 shows the effect of temperature on the flux and rejection

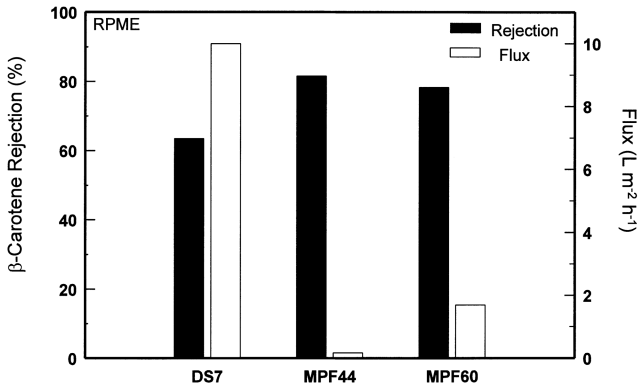

FIG. 1. Performance of membranes tested with red palm methyl esters. Pressure was 2.76 MPa, temperature was 40°C.

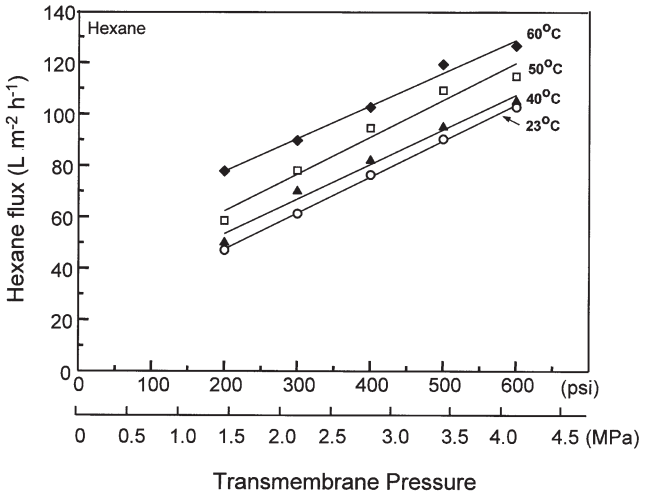

FIG. 2. Effect of temperature and transmembrane pressure on hexane flux with the DS7 membrane.

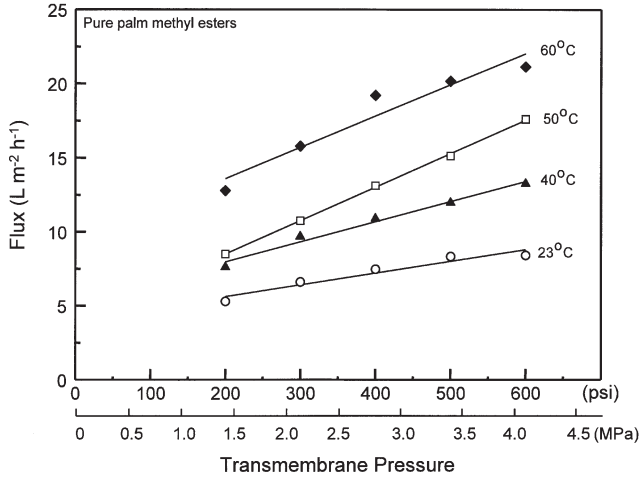

FIG. 3. Effect of temperature and transmembrane pressure on the flux of pure palm methyl esters with the DS7 membrane.

of RPME at 4.2 MPa (600 psi) and VCR 2. Flux increased linearly from 5.5 L m^{-2} h^{-1} at 23°C to 17.4 L m^{-2} h^{-1} at 60°C. However, the rejection decreased as the temperature increased. This could be because the higher temperature caused an increase in diffusivity, allowing the carotene to diffuse at a higher rate, or it could be due to swelling of the membrane at higher temperatures, resulting in an increase in pore size. Figure 4 suggests that the best combination of high flux and high rejection is 40°C.

Effect of concentration with RPME. Figure 5 shows results of a concentration experiment with a feed solution containing an initial carotene concentration of 0.45 g L^{-1}. The carotene concentration increased from 0.45 g L^{-1} in the feed to 1.88 g L^{-1} at VCR 10. This is an increase of about four times the original carotene concentration in the feed. The permeate initially contained approximately 0.2 g L^{-1} carotenes and increased to 0.3 g L^{-1} at VCR 10. The rejection increased from 74% at VCR 1 (0.45 g L^{-1} carotene in feed) to 80% at VCR 10 (1.8 g L^{-1} carotene), as shown in Figure 6. Ideally, the rejections should have been close to 100% since the DS7 is rated by the manufacturer as 400 MWCO and the M.W. of β-carotene is 536. The lower rejection of carotenes could be attributed to the shape or geometry of the molecule. Carotene ($C_{40}H_{56}$) is a linear unsaturated aliphatic chain with a benzene ring at each end. This makes it possible for the molecule to pass through membranes with a smaller nominal pore size.

In addition, the MWCO is only a nominal number provided by manufacturers using specific test solutes. The rejection characteristics of NF membranes depend on the solute and the solvent. The MWCO profile of NF membranes was different in organic solvents compared with water (17). A low rejection of carotene was also reported by Koseoglu *et al.* (8), but the mechanism would be different since their membranes also allowed the passage of oil, which has a higher M.W. than carotene.

Figure 6 also shows the flux during the concentration experiments. The data in this figure were used to obtain empirical relationships between flux (J in L m^{-2} h^{-1}), rejection of β-carotene (R), and carotene concentration in the retentate (C_R, g L^{-1}) at a pressure of 4.2 MPa and 40°C. These are shown in Equations 1 and 2:

$$J = 6.5 - 0.197 \ln C_R \quad [1]$$

$$R = 77.9 + 3.86 \ln C_R \quad [2]$$

These models were used for the preliminary process design and economic calculations presented next.

Process design and economics. Since the average rejection of β-carotene by the DS7 membrane is 74–83%, a multistage

TABLE 2
Permeability of Hexane and Methyl Esters (ME) with DS7 Membrane at 2.76 MPa And Various Temperatures[a]

Temperature (°C)	Permeability (L m^{-2} h^{-1}/MPa)		Relative permeability of hexane/ME
	Hexane	ME	
23	27.7	2.7	10.3
40	29.7	3.9	7.5
50	34.7	4.8	7.2
60	37.2	7.0	5.3

[a]Permeability values were obtained from the slopes of the plots in Figures 2 and 3.

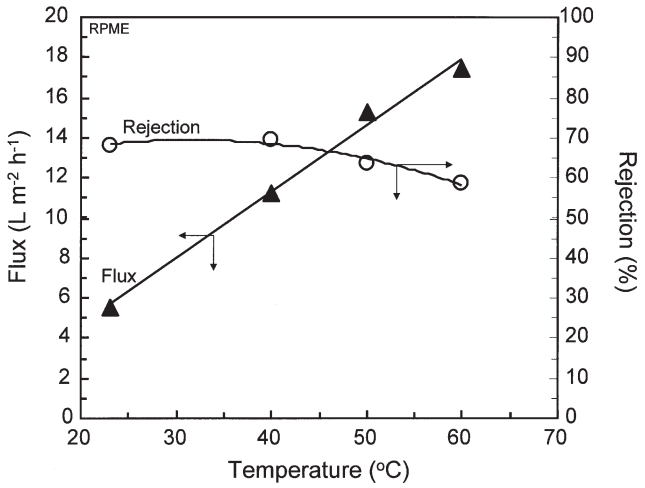

FIG. 4. Effect of temperature on the flux and rejection of red palm methyl esters (RPME) with the DS7 membrane. Data measured at a volume concentration ratio (VCR) of 2 and pressure of 4.2 MPa.

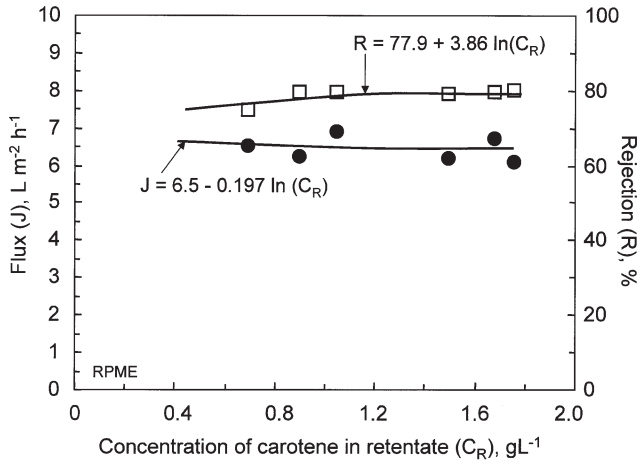

FIG. 6. Flux and rejection of the DS7 membrane during concentration of RPME at 40°C and 4.2 MPa. For abbreviation see Figure 4.

membrane process would be required to separate the β-carotene from the palm methyl esters, in which the permeate from the initial separation step is sent through successive membrane stages.

Figure 7 shows a three-stage process with a feed flow rate of 10 tons per hour (11,111 L h^{-1}) of RPME. Table 3 shows the calculation for each stage of the process and its corresponding membrane area and cost, based on the process design suggested by Cheryan (6).

The first stage is operated at VCR 10 with a fresh RPME feed of 11,111 L h^{-1}. The carotene concentration of the feed into the first stage is 0.45 g L^{-1}. The retentate from stage 1 has a flow rate of 1,111 L h^{-1} at a carotene concentration of 1.85 g L^{-1}. The permeate from stage 1 is processed in stage 2 to VCR 10 to produce 1,000 L h^{-1} of retentate with a carotene concentration of 1.21 g L^{-1}. At stage 3, the permeate from stage 2 is concentrated to VCR 6 to produce 1,500 L h^{-1} of retentate with 0.79 g L^{-1} of β-carotene and 7,500 L h^{-1} of permeate containing 0.096 g L^{-1} of β-carotene.

By applying this multistage mode, two final products leave the membrane system: a carotene concentrate at 3,611 L h^{-1} with 1.19 g L^{-1} carotene, and a refined palm methyl ester stream at a flow rate of 7,500 L h^{-1} with 0.096 g L^{-1} carotene. The sum of these two products should be the same as the feed flow rate to the first stage. The yield of carotene in the final concentrate is 85.6% of the carotene in the feed. The rest of the carotene remains in the permeate at a concentration of 0.096 g L^{-1}. It is possible to recover the carotene in the permeate, but to be economical, this would require a membrane with higher rejection and flux. For example, a membrane with 99% rejec-

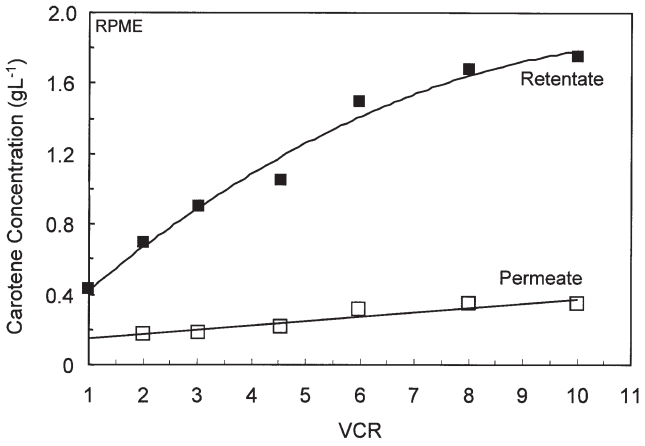

FIG. 5. Concentration of RPME with the DS7 membrane at 40°C and 4.2 MPa. For abbreviations see Figure 4.

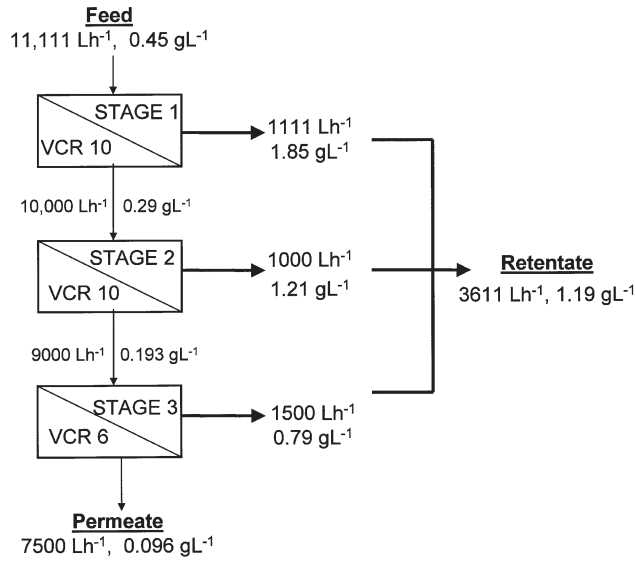

FIG. 7. Design of a multistage membrane separation process for recovering carotene from RPME. For abbreviations see Figure 4.

TABLE 3
Cost Calculation of a Multistage Membrane Process to Process 10 Tons per Hour of Red Palm Methyl Esters[a]

	Stage			
	1	2	3	Total
Feed (ton/h)	10.0			
Feed density	0.9	0.9	0.9	
Feed (L h^{-1})	11,111	10,000	9,000	
Carotene concentration in feed (g L^{-1})	0.45	0.294	0.193	
VCR[b]	10	10	6	
Rejection	0.80	0.79	0.75	
Carotene in retentate (g L^{-1})	1.85	1.21	0.675	
Carotene in permeate (g L^{-1})	0.294	0.193	0.096	
Retentate flow (L h^{-1})	1,111	1,000	1,500	
Permeate flow (L h^{-1})	10,000	9,000	7,500	
Flux (L m^{-2} h^{-1})	6.08	6.08	6.18	
Area of membrane (m^2)	1,645	1,480	1,214	4,339
Membrane replacement cost ($/$m^2$)	170	170	170	
Membrane plant cost ($/$m^2$)	500	500	500	
Membrane plant cost ($)	822,000	740,000	607,000	2,169,000
Depreciation @ 10% ($/yr)	82,000	74,000	61,000	217,000
Operating cost @ 33% ($/yr)	274,000	247,000	202,000	723,000
Total processing cost ($/yr)				940,000
Carotene produced (kg/yr)				25,700
Carotene yield (%)				85.6
Carotene processing cost ($/kg)				37

[a]Operating hours per year = 8000; costs based on 2005 prices for utilities in the U.S. Midwest; capital and operating costs based on calculations in Reference 6.
[b]VCR, volume concentration ratio.

tion of β-carotene would require only two stages of VCR 10 each to recover 99.3% of the β-carotene.

Table 3 also shows the costs of the membrane process. We assumed that the commercial plant will utilize cross-flow spiral-wound membrane modules. A spiral-wound plant for aqueous applications is budget-priced at $300/$m^2$ and the membrane replacement cost is $50–100/$m^2$ (6). Since this is a solvent-based membrane plant rather than being aqueous-based, the membrane plant budget cost has been increased to $500/$m^2$ and the membrane replacement budget cost to $170/$m^2$ (personal communications with Koch Membrane Systems, Wilmington, MA, and MTR, Menlo Park, CA). The operating cost accounts for electrical power, cleaning, and annual membrane replacement; it generally averages about one-third of the capital cost for spiral-wound membranes (6). The total processing cost based on operating cost and depreciation was $37/kg of pure carotene in the concentrate, which is far less than the current selling price of $640/kg (on a 100% basis) for synthetic carotene (18).

The process design was based on data obtained in a small laboratory dead-end stirred cell. Commercial membrane plants are continuous and operate on the cross-flow principle, which should result in better control of concentration polarization and fouling (6), leading to lower membrane areas and cost. The carotene concentrate needs to be evaporated or distilled to obtain a more concentrated carotene product. However, the volume to be distilled has now been reduced by 67%, since the carotene concentrate stream is only one-third of the initial feed volume. In addition, carotene is not the only product in this process. Glycerol is produced during the transesterification, and methyl esters are produced during NF. The methyl esters are of high quality since it is already substantially decolorized. These coproducts enhance the potential profitability of the process.

ACKNOWLEDGMENTS

This study was partly supported by the Illinois Agricultural Experiment Station, University of Illinois. The authors acknowledge the Indonesian Oil Palm Oil Research Institute for the leave and scholarship provided for D. Darnoko, and GE-Osmonics and Koch Membrane Systems for providing the membranes.

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[Received May 18, 2005; accepted December 16, 2005]