Separation of Fatty Acids/Triacylglycerol by Membranes

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ABSTRACT: Separation of fatty acids from triacylglycerol by membrane separation technique has been studied. Mixtures of triacylglycerols and fatty acids were extracted with alcohol, and the alcohol extracts were treated for recovery of oil by membrane separation technique. The membranes used were of both cellulosic and noncellulosic types. Polyamide membranes showed better selectivity toward fatty acid separation as compared to cellulose acetate and polysulfone membranes. For groundnut oil/fatty acid/alcohol mixture and a polyamide membrane, the free fatty acid (FFA) concentration in the permeate was 86.82% at 0.7 MPa pressure when the feed had 61.71% FFA. A reasonable permeate flux of 67.36 $lm^{-2}h^{-1}$ was obtained. Results obtained have been useful in selecting membrane material suitable for such applications.
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KEY WORDS: Alcohol solubility, cellulosic and noncellulosic membranes, deacidification, hydrophobic/hydrophilic, liquid–liquid extraction, mixed fatty acids, polyamide, polysulfone, reverse osmosis, triacylglycerol, ultrafiltration.

Applications of membrane separation processes in the oils and fats industry have recently attracted a great deal of attention. A considerable amount of exploratory work has been done in the areas of hexane recovery from oil miscella, vapor recovery, condensate return, degumming, refining and bleaching, hydrogenation catalyst recovery, waste-water treatment, and others (1). In allied industries, membrane separation has found good application in recovery and purification of protein (2). Membrane processes have been investigated primarily for their energy efficiency and selectivity. Deacidification of oils and fats is most widely done by alkali refining. Physical refining has also been suggested as a possible replacement for alkali refining. The relative merits and demerits of these two processes have been summarized excellently by Norris (3). The ultrafiltration (UF) process is already well recognized as a pretreatment step for physical refining. Further work in this area seems to be necessary. Deacidification by membrane processes has been tried with a combination of a hydrophobic/hydrophilic membrane system (4) and by liquid–liquid extraction in a membrane extractor (5). In the former case, the problem of soap disposal still remains, and an exotic solvent had to be used in the latter. The mechanism for separation in both cases was diffusion controlled, as evidenced from the large molecular weight cut-off (MWCO) employed. A membrane separation process also has been suggested in ethanol extraction of cottonseed, and separation data have been presented for systems involving isopropyl alcohol, ethanol, and hexane (6).

In the present work, attempts have been made to separate fatty acids and triglycerides from the extract phase that is obtained from alcoholic extraction of high-free fatty acid (FFA) oils.

EXPERIMENTAL PROCEDURES

Materials and methods. Mixed fatty acids were prepared from refined groundnut oil (M/s. Godrej Soaps Ltd., Bombay, India) by complete saponification and acidulation. Model mixtures of test samples were prepared by blending mixed fatty acids with refined groundnut oil in different proportions. Reagents and solvents used were of analytical reagent-grade (equivalent to BDH analar grade). Solvents were redistilled prior to use. Different test samples as feed for various experiments were made by the following procedure: (i) a 10% (wt/vol) solution in ethanol with oil and fatty acids in the ratio of 70:30, (ii) a 10% (wt/vol) solution in ethanol with oil and fatty acids in the ratio of 40:60; and (iii) in another experiment, rice bran oil with an FFA content of 34% was degummed with phosphoric acid, and excess phosphoric acid and sludge were removed by adding calcium carbonate. Degummed oil was dissolved in ethanol as a 15% (wt/vol) solution. All samples thus prepared were clear solutions, and no separation of oil was observed.

Acid value, saponification value, and acylglycerol contents (mono-, di-, and tri-) were determined according to International Union of Pure and Applied Chemists methods II.D.1, II.D.2, and II.C.7, respectively (7). The membranes used were cellulose acetate, polysulfone, and polyamide. Cellulose acetate membranes were obtained from Amafilter Membrane Technik GmbH, (Hanover, Germany), and polysulfone and polyamide membranes were procured from Bhabha Atomic Research Centre (B.A.R.C.) (Bombay, India).

A reverse osmosis/UF test rig from Patterson Candy International (Whitchurch, Hampshire, United Kingdom), was suitably modified to accommodate a test cell from Amafilter with cross-flow configuration. The motor of the pump and

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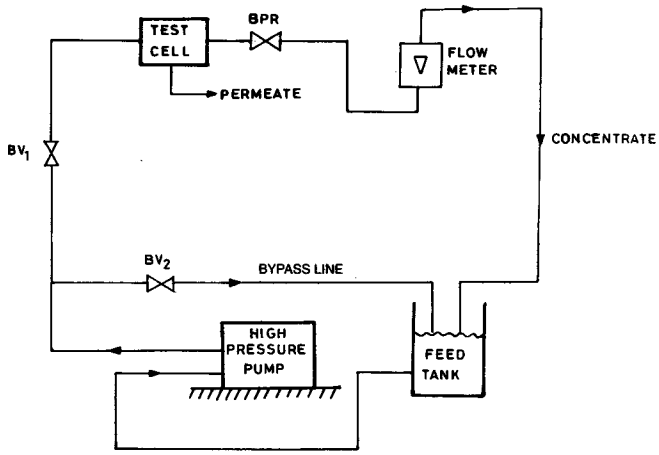

FIG. 1. Flow diagram of the system. BPR, back pressure regulating valve; BV_1, needle valve (feed line); BV_2, needle valve (by-pass line).

other electrical installations were explosion-proof and confirmed to the specifications of the Indian School of Mines (Dhanbad, India). A flow diagram for the test's system is shown in Figure 1.

RESULTS AND DISCUSSION

Membranes employed had an MWCO between 500–1000D, so that the pressure requirements were not high. Results indicated that, apart from fatty acid and oil contents of the feeds, the presence of polar components, such as monoacylglycerols and diacylglycerols, had a profound effect on separation. Hexane is an ideal solvent for both triacylglycerol and fatty acids, but hexane-resistant membranes with reasonable fluxes are not available for the separation of fatty acids from oil. More commonly-available membranes with low MWCO (around 500–1000D) are quite compatible with alcohol because of their general hydrophilic nature. However, triacylglycerols have a limited solubility at room temperature in ethanol. The extract phase obtained from alcoholic extraction of a high-FFA oil will contain some quantity of triacylglycerol, but remains clear due to the presence of a large quantity of fatty acids in solution. Multiple extraction leads to higher oil losses. Recovery of oil from the extract phase has, therefore, been suggested in the present study. The general characteristics of membranes used are given in Table 1. The pure water permeability constants (PWPC) for each membrane were also determined. This is an important parameter for membrane selection because these data are independent of the solute used. For the cellulose acetate membrane, the PWPC values indicated that, at higher pressure, the compaction effect (creeping of membrane material) was noticeable. There polysulfone membrane showed a continuous rise in PWPC over the pressure range employed, presumably because of its high MWCO (8). However, the polyamide membrane maintained PWPC values at a fairly constant level over the range of applied pressure (Fig. 2). This information is useful for predicting the behavior of the membrane material for the intended application. The results obtained for the cellulose acetate membrane indicated that the separation of fatty acids from triacylglycerols remains virtually unaffected over the entire range of pressure tested, although a decline in flux was observed. This is due to the compaction effect at higher pressure, as mentioned earlier. For the polysulfone membrane, the flux increase is rapid, and separation obtained was not encouraging. With the polyamide membrane, a fairly good separation was achieved, along with a reasonable flux (Fig. 3). These results are, therefore, indicative of the suitability of polyamide membranes for the given task. For degummed rice bran oil with a high FFA content and the cellulose acetate membrane, with increased feed pressure, the permeate flux increased sharply with a decrease in fatty acid selectivity. The result obtained indicates that this oil behaved differently than the model mixtures of groundnut oil and groundnut oil mixed with fatty acids (Fig. 4). This may be attributed to the presence of highly polar components, such as mono- and dia-

TABLE 1
General Characteristics of the Membranes

	Cellulose acetate	Polysulfone	Polyamide
Molecular weight cut-off	500D	1000D	500–600D
pH tolerance	1–13	1–14	2–11
Temperature tolerance	50°C	up to 70°C	up to 50°C
Pressure limits with pure water	5–7 bar	—	5—7 bar

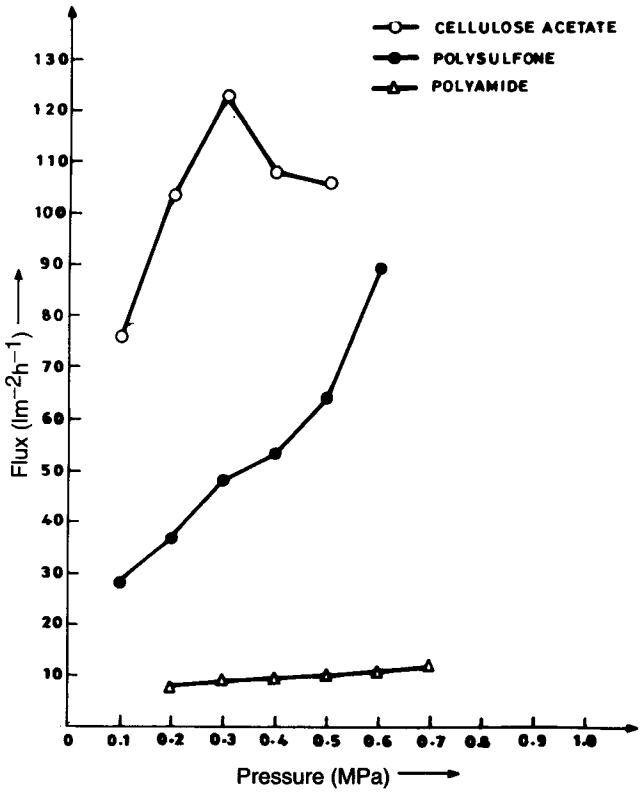

FIG. 2. Pure water permeability constants of the membranes.

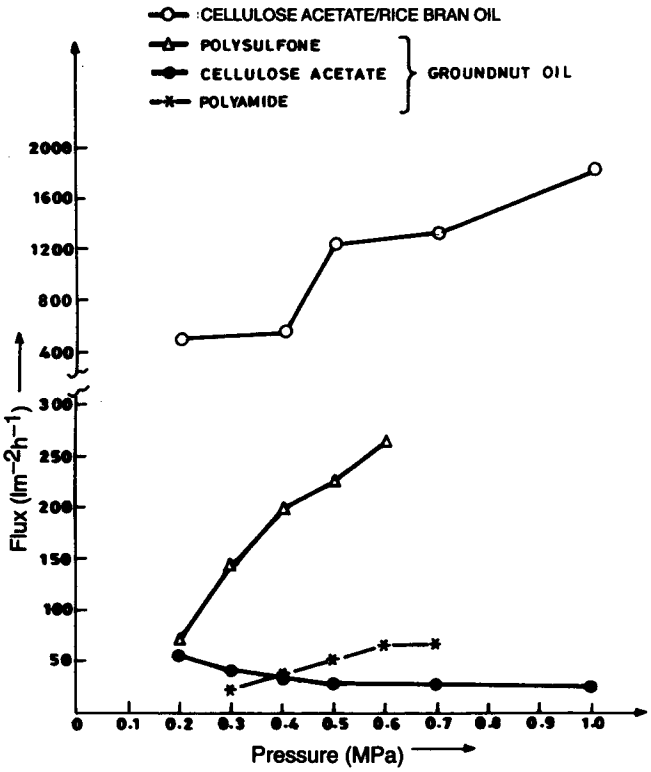

FIG. 3. Pressure vs. flux for the actual mixture.

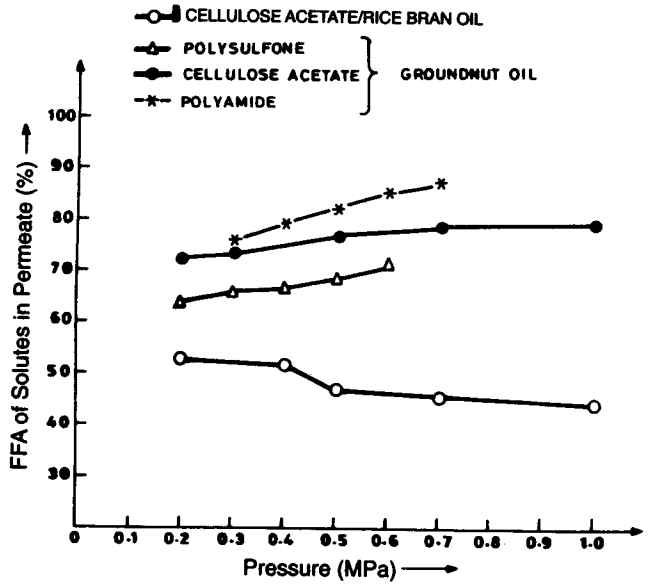

FIG. 4. Pressure vs. free fatty acids (FFA) in permeate for the actual mixture.

cylglycerol, in the oil, which may interact preferentially with the membrane material (9).

Based on these observations, we conclude that polyamide membranes are better suited for the separation of fatty acids and triacylglycerol. This is due to the fact that polyamide membranes are slightly less hydrophilic, and they are less prone to compaction compared to cellulose acetate. The overall aim is to achieve the desired separation at low applied pressure (preferably below 20 bar) because capital and other attending costs increase with operating pressure.

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