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Ultrafiltration of oil-in-water emulsion: Comparison of ceramic and polymeric membranes

Gyula N. Vatai[a*], Darko M. Krstić[b], András K. Koris[a], Igor L. Gáspár[a], Miodrag N. Tekić[c]

[a]*Department of Food Engineering, Corvinus University of Budapest, Ménesi st. 44, H-1118 Budapest, Hungary*
Tel. +36 (1) 482-6232; Fax. +36 (1) 482-6323; email: gyula.vatai@uni-corvinus.hu
[b]*Novel Technologies (Malta) Ltd., Zinja No. 2, Triq il-Kappara, MSK 3300 Marsascala, Malta*
email: info@novelmalta.com
[c]*Faculty of Technology, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia*
email: mntekic@uns.ns.ac.yu

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ABSTRACT

Ultrafiltration (UF) has been recognized as a highly attractive technique for the treatment of stable oil-in-water emulsions. This technique has proved to be more effective then conventional methods since it may produce a water phase of higher quality and an oil phase which can be recycled. However, low permeate fluxes due to membrane fouling still represent one of the main limitations for its extensive application. The aim of this paper is to further contribute to the investigations of mass transfer characteristics during UF of oil-in-water emulsions. The performance of a polymeric (polyaryletherketone) membrane and a ceramic (zirconia) membrane were compared under different parameters of the UF process. The permeate recirculation experiment showed that the ceramic membrane is sensitive to oil penetration at lower cross-flow velocities and higher transmembrane pressures. The optimal performance for the ceramic membrane was obtained at a lower feed flow rate and transmembrane pressure compared to the optimal values for the polymeric membrane. The comparison experiments with volumetric concentration of the feed were carried out at optimal operation conditions for each of the membranes in order to maximise their performance. While the polymeric membrane showed expected oil rejection variation consistent with surface layer formation, the ceramic membrane showed poor oil rejection at the beginning of the operation. Further investigations need to show if the poor initial oil rejection of the ceramic membrane can be reduced without losing proved advantages of ceramic membranes over polymeric membranes.

Keywords: Cross-flow ultrafiltration; Oil-in-water emulsion; Polyaryletherketone; Zirconia

1. Introduction

Oil-in-water emulsions are generated by various industries and subsequently discharged into the natural environment creating a significant ecological problem. The conventional methods for treatment of oil-in-water emulsions can be classified as chemical, mechanical and thermal. However, these methods have shown several disadvantages such as low efficiency, operational difficulties and high operation costs. To address this problem,

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*Corresponding author.

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membrane processes, such as microfiltration, ultrafiltration (UF), nanofiltration and reverse osmosis have been investigated. These processes have proved to be more effective than conventional methods because they can produce a water phase of higher quality and oil phase which can be recycled at low operating costs. UF, especially a cross-flow mode of operation, has been extensively investigated. For more than 25 years, this process has been considered as an attractive method for the separation of stable oil-in-water emulsions. The use of cross-flow UF employing both polymeric and ceramic membranes has been reported in many articles [1–8]. Nevertheless, membrane fouling that leads to permeate flux decline and reduced membrane selectivity has been recognised as a main limitation of this process. Oil-in water emulsions induce three types of fouling mechanisms: oil droplet deposit, concentration polarisation and adsorption of dissolved organic compounds [9].

In order to reduce membrane fouling and to improve permeate flux, different approaches have been investigated, including changing of operating conditions [10], alteration of membrane material characteristics [11,12] and using of different hydrodynamic methods such as air sparging [7,9], high-shear rotary UF [13] or insertion of static turbulence promoters [14]. Howell [10] has introduced a concept of critical flux suggesting filtration at low transmembrane pressure as a method for reduction of membrane fouling during microfiltration. This investigation showed that operation below certain values of the transmembrane pressure (TMP) can eliminate or significantly reduce membrane fouling, leading to improved process performance over time despite low permeate flux values. Faibish and Cohen [11] have reported the increase of over 20% in oil rejection for a commercial cutting oil emulsion with a polymer-modified zirconia-based UF membrane compared to the native membrane. Ju at el. [12] have reported high flux increase and higher organic rejection in the case of a coated polysulfone membrane compared to the uncoated membrane. Viadero Jr. et al. [13] have shown that high-shear rotary UF allows concentration of oil beyond the typical operating limitations of conventional UF modules. Krstic et al. [14] have shown that the operation conditions should be selected properly in order to achieve significant increase in permeate flux with reduction in operating costs during UF with inserted static mixer as a turbulence promoter.

Ceramic membranes have been extensively investigated for the treatment of oil emulsions. Ceramic membranes have gained popularity due to their better mechanical, thermal and chemical stability over polymeric membranes. However, the hydrophobic nature of the ceramic membranes, high price and limited availability of pore size range are identified as their main disadvantages over polymeric membranes. The reported results [3,5] suggest that high pressure and high velocity represent the optimum operating conditions for a polymeric membrane. On the other hand, the fouling phenomena of ceramic membranes are very affected by the TMP; therefore, the operation at a moderate pressure has been recommended [8,14].

The aim of this study was to compare the performance of a ceramic and a polymeric membrane during UF of an oil-in-water emulsion. It was assumed that the membrane performance could significantly vary with operation conditions. In that case, comparison at the same operation condition could "mask" the actual membrane performance. Therefore, the optimal operation conditions for both membranes were determined during permeate recirculation experiments, followed by volumetric concentration experiments carried out at genuine optimal operating conditions for both polymeric and ceramic membranes.

2. Materials and methods

The experiments were carried out in cross-flow mode using a conventional UF set-up with two modules installed: tubular single-channel module containing a ceramic zirconia (ZrO_2) membrane (Pall Exekia, BP1, Bazet, France) and a flat sheet polymeric polyaryletherketone (PAEK) membrane (BFM 70100-P, Berghof, Germany) (Fig. 1). The ceramic membrane used had a nominal pore size of 20 nm, diameter of 6.8 mm and an effective membrane area of 46.2 cm^2, while the polymeric membrane had a molecular weight cut-off (MWCO) of 100 kDa and an effective membrane area of 470 cm^2.

A stable oil-in-water emulsion was prepared from a non-used water-soluble cutting oil (Unisol, MOL, 1117 Hungary). The oil concentration in the emulsion was 5% (w/w). All experiments were carried out at 50 °C. The

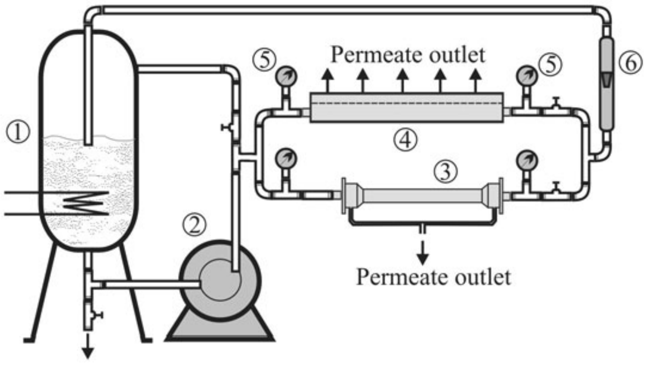

Fig. 1. Schematic diagram of the experimental set-up. 1 feed tank, 2 circulation pump, 3 ceramic ZrO_2 membrane, 4 polymeric PAEK membrane, 5 pressure gauge, 6 liquid flow meter.

density and dynamic viscosity of used emulsion were $\rho = 992.3$ kg m^{-3} and $\mu = 1.278\times10^{-3}$ Pa s, respectively. The feed was pumped from a tank to the membrane module and then recirculated. The volume flow rate (Q) and TMP were controlled by means of regulation valves. The liquid flow rate was varied from 75 to 500 L h^{-1}. The cross-flow velocity was calculated as a superficial velocity. The volumetric concentration factor (VCF) during concentration of the emulsion was determined as the ratio of feed volume at the beginning of operation ($V_{feed,i}$) to retentate volume in time t ($V_{ret,t}$):

$$VCF = \frac{V_{feed,i}}{V_{ret,t}} \tag{1}$$

The membranes were cleaned according to the recommendations of the manufacturers prior to each experiment and the pure water fluxes of the cleaned membranes were measured. The cleaning procedure was repeated until the original water flux was restored.

Beside permeate flux, one of the most important parameters from an economical point of view is the specific energy consumption (E) defined as the power dissipated per unit volume of permeate. The hydraulic dissipated power is directly related to the pressure drop along the membrane module (ΔP) and the specific energy consumption can be calculated as:

$$E = \frac{Q\cdot\Delta P}{J_p\cdot A} \tag{2}$$

where J_p is the permeate flux and A is the membrane surface area.

The oil concentrations in the feed and the permeate solutions were analyzed using UV spectrophotometer (Spectronic Genesys 5, Milton Roy, USA).

3. Results and discussion

3.1. Permeate recirculation experiments

The influence of operation conditions, namely TMP and feed flow rate (cross-flow velocity) on the process performance, was investigated during recirculation of the permeate to the feed tank. Operation temperature was set to be 50°C due to thermal limitation of the PAEK membrane. Optimal operation conditions for both ceramic and polymeric membranes were determined by taking into account productivity (permeate flux), energy consumption (specific energy consumption) and membrane selectivity (oil content in the permeate).

The ceramic membrane module had better hydrodynamic characteristics providing the same cross-flow velocities at lower feed flow rates compared to the polymeric membrane. Therefore, in order to compare flux values of both membranes at the same cross-flow velocities, the ceramic membrane experiments were carried out at lower feed flow rates. The obtained pseudo-steady state values of the permeate flux are shown in Fig. 2.

The permeate flux values were slightly higher in the case of the ceramic membrane. Similar flux variation with TMP was observed for the both membranes; increase of the flux with increase of a TMP to a certain value when a "limiting flux" was reached. The dotted lines in Fig. 2 represent an indication of the border between pressure controlled and mass-transfer controlled regions. Higher values of the limiting flux were obtained in the case of the ceramic membrane, especially at higher TMP values. This "extension" of the pressure controlled region and slightly higher flux values can be explained by the bigger pore size of the ceramic membrane compared to the pore sizes of the polymeric membrane.

Fig. 2 shows that higher TMPs and flow rates provide higher flux values. However, this is accomplished at the expense of higher energy consumption. Therefore, in order to determine optimal operation conditions, energy consumption, usually expressed as specific energy consumption (E), was determined for both membranes. The obtained results are presented in Fig. 3.

The difference between energy consumption of the examined membranes can be explained by the membrane module configuration. The polymeric membrane was a flat-sheet type with the membrane area of almost 10 times of the single-tube ceramic membrane area. The ceramic membrane module could produce the same cross-flow velocity at lower flow rates with lower pressure drop along the membrane length. However, despite its better hydrodynamic characteristics, the flat type polymeric membrane module had lower ratio of pressure drop along the membrane to filtered volume due to much higher filtered volume capacity compared to the one of the ceramic membrane module, which, according to Eq. (2), resulted in lower E values at the same TMP and cross-flow velocity (Fig. 3).

The results presented in Figs. 2 and 3 suggest that a flow rate of 150 L h^{-1} (1.2 m s^{-1}) and a TMP of around 150 kPa can be considered as an optimum in the case of the ceramic ZrO_2 membrane. Operation at higher flow rates would not be economically feasible for this module configuration due to high energy consumption. The polymeric membrane showed that the specific energy consumption as low as 2 kWh m^{-3} can be obtained at flow rates of up to 300 L h^{-1} (1.8 m s^{-1}) and this value of the flow rate can be chosen as an optimal value. The limiting flux at

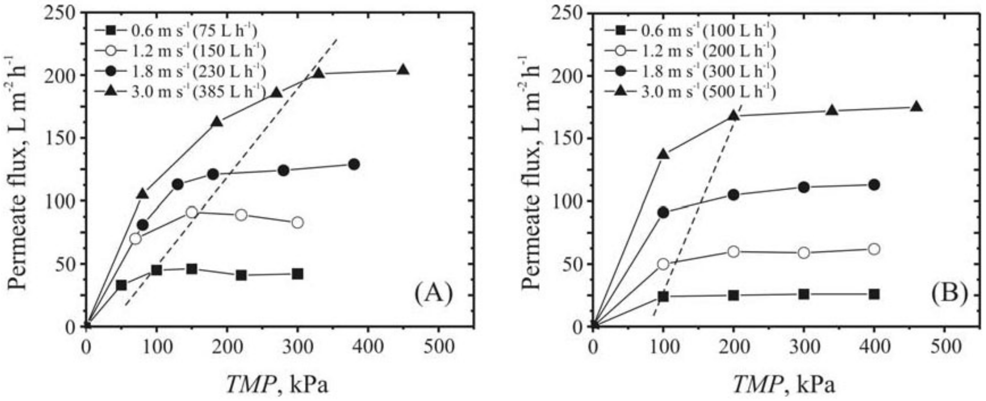

Fig. 2. Variations of the permeate flux with TMP at various cross-flow velocities (feed flow rates). Membrane type: (A) ceramic ZrO_2; (B) polymeric PAEK.

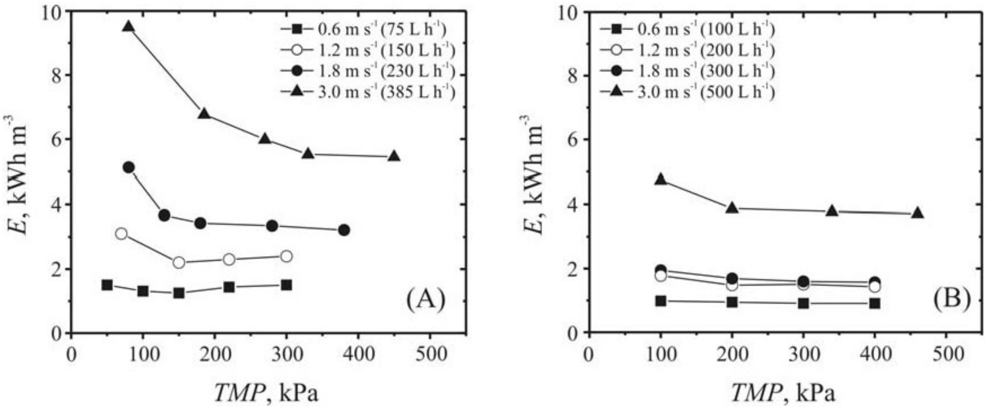

Fig. 3. Specific energy consumption vs. TMP at various cross-flow velocities (feed flow rates). Membrane type: (A) ceramic ZrO_2; (B) polymeric PAEK.

the flow rate of 300 L h^{-1} was achieved at a *TMP* of around 200 kPa.

Beside high flux and low energy consumption, the third main characteristic which determines the membrane performance is the membrane selectivity. Therefore, the optimal operation conditions should also provide good membrane separation properties. Membrane separation properties were expressed as an oil concentration in the permeate. Any value of oil concentration below 50 mg L^{-1} (limiting value for discharge to the public sewer in Hungary [15] was considered as acceptable). The permeate oil concentrations in the case of the polymeric PAEK membrane were in a range from 80 to 220 mg L^{-1} for the examined operation conditions. The changing of operating conditions did not produce any significant influence on the separation properties of this membrane. On the other hand, the separation properties of the ceramic membrane were strongly influenced by the operation conditions and the obtained permeate oil concentrations at various TMP and velocities are shown in Table 1.

Table 1
Separation characteristics of the ceramic ZrO2 membrane at different TMP and cross flow velocities (flow rates). In bold letters: values lower than 50 mg L^{-1}

TMP [kPa]	Oil concentration in the permeate [mg L^{-1}]			
	Cross-flow velocity (Volumetric flow rate)			
	0.6 m s^{-1} (75 L h^{-1})	1.2 m s^{-1} (150 L h^{-1})	1.8 m s^{-1} (230 L h^{-1})	3.0 m s^{-1} (385 L h^{-1})
50	**42**	**8**	**16**	**6**
100	105	**17**	**11**	**21**
150	152	**21**	**39**	**29**
200	>1000	515	250	128
300		>1000	370	732
400			>1000	>1000

The results in Table 1 clearly indicate that the ceramic membrane is sensitive to oil penetration at lower cross-flow velocities and higher TMPs. However, in the cases of moderate TMPs (values in bold), the oil rejection was very good and the oil concentration in the permeate were much lower than the values obtained with the polymeric membrane. The final choice of the optimal operation conditions has to take into account all results presented in Table 1 and Figs. 2 and 3. Table 2 presents a summary of the previous results, showing the limiting flux values, together with corresponding TMP, *E* and permeate oil concentration, for both membranes at different cross-flow velocities.

Highlighted rows of the Table 2 represent the most favourable membrane performance taking into consideration membrane productivity, energy consumption and selectivity. The optimal operation conditions were chosen to be: a flow rate of 150 L h^{-1} (1.2 m s^{-1}) and a TMP of 150 kPa for the ceramic ZrO_2 membrane and a flow rate of 300 L h^{-1} (1.8 m s^{-1}) and a TMP of 200 kPa for the polymeric PAEK membrane.

Table 2
Membrane performance at different operating conditions

Ceramic membrane				
Cross-flow velocity [m s^{-1}]	TMP_{lim} [kPa]	$Flux_{lim}$ [L m^{-2} h^{-1}]	E_{lim} [kWh m^{-3}]	Permeate oil conc. [mg L^{-1}]
0.6	100	45	1.3	105
1.2	150	90	2.2	21
1.8	180	120	3.4	39–250
3	320	200	5.6	732–1000
Polymeric membrane				
Cross-flow velocity [m s^{-1}]	TMP_{lim} [kPa]	$Flux_{lim}$ [L m^{-2} h^{-1}]	E_{lim} [kWh m^{-3}]	Permeate oil conc. [mg L^{-1}]
0.6	100	25	1	80-220
1.2	200	60	1.5	
1.8	200	100	1.7	
3	200	170	3.9	

3.2. Volumetric concentration of oil-in-water emulsion

Volumetric concentration of the feed solution was carried out at actual operation conditions for each of the tested membranes. The variations of permeate flux and specific energy consumption are shown in Fig. 4, while Fig. 5 shows the variation of the permeate oil concentration during feed concentration.

Fig. 4 shows that similar values of the permeate flux and the energy consumption were obtained despite the ceramic membrane being operated at 50% lower cross-flow velocity and around 30% lower TMP compared to the operating conditions of the polymeric membrane. Although efficient operation at lower velocities and pressures certainly is in favour of the ceramic membrane, this membrane showed unexpectedly poor oil rejection during feed concentration experiments (Fig. 5). Different patterns of the variations of the oil concentrations indicate different membrane fouling mechanisms [16]. The polymeric membrane showed expected oil rejection variation consistent with formation of the surface layer of the oil droplets, while the ceramic membrane showed poor oil rejection at the beginning of the operation (up to VCF of 1.5). To confirm this, Fig. 6 shows the oil concentration in the permeate samples taken during the both experiments.

Moderate variations of the oil concentrations in the permeate samples for the polymeric membrane proves that the surface layer and the concentration polarisation determine the membrane rejection properties. Contrary to the polymeric membrane, the ceramic membrane showed poor oil rejection at the beginning of the operation. After initial oil penetration, the membrane showed continuous increase in oil rejection, slowly approaching the values for the polymeric membrane. It can be assumed that the hydrophobic nature and the bigger pore sizes of the ceramic membrane facilitated initial oil permeation. One of the approaches is to coat a ceramic membrane with a polymeric layer. Wang et al. [17] coated a porous ceramic membrane with the polyamide/PVA composite thin top-

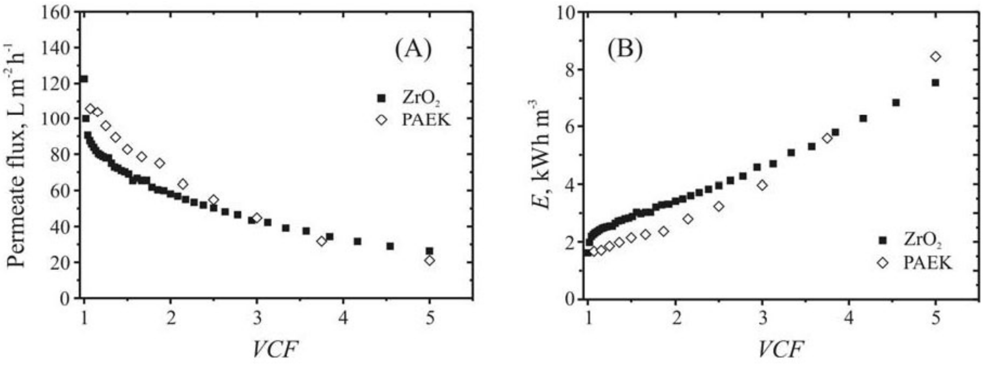

Fig. 4. Permeate flux (A) and specific energy consumption (B) as a function of VCF for the ceramic ZrO2 and polymeric PAEK membranes.

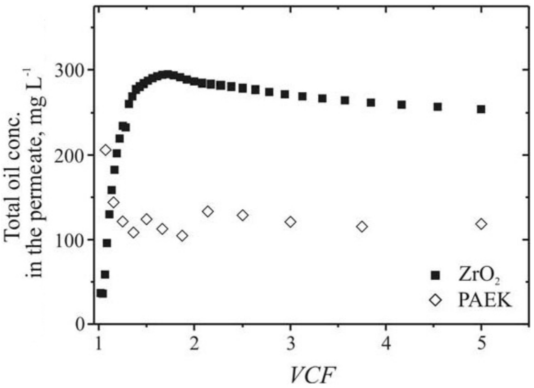

Fig. 5. Total oil concentration in the permeate vs. VCF for ceramic ZrO_2 and polymeric PAEK membranes.

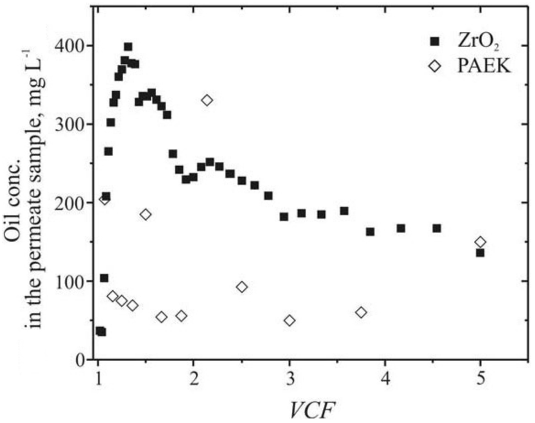

Fig. 6. Oil concentration in the permeate sample vs. VCF for ceramic ZrO_2 and polymeric PAEK membranes.

layer. The prepared membrane showed a good performance for treating the O/W microemulsions with a mean diameter of about 2.4 μm; the oil rejection was always higher than 98.5% from the beginning throughout the operation. However, since the polymer coating of the ceramic membranes diminishes the major advantages of ceramic membranes such as thermal and chemical resistance, modification of a ceramic membrane itself appears as an interesting solution [18,19]. Our results suggest that initial oil penetration through the ceramic membrane could be reduced if the experiment is performed in the recirculation mode until the surface layer is formed and the pseudo-steady-state conditions are reached. A more practical approach could be alteration of the system hydrodynamics in such way to drag away the large oil droplets from the membrane surface. Use of centrifugal force has already proved effective for achieving a high VCF of oil emulsions [13]. Our volumetric concentration experiments showed one of the advantages of the ceramic membrane over the polymeric membrane; similar permeate fluxes were obtained at similar energy consumption but at significantly lower cross-flow velocity and TMP. Further investigations will show if the poor oil rejection of the ceramic membrane at the beginning of the operation can be reduced without losing proved advantages of ceramic membranes over polymeric membranes.

4. Conclusions

The comparison experiments certainly showed the advantage of the ceramic membrane over the polymeric one in the area of membrane productivity. Bigger pore sizes with better module hydrodynamics provided similar permeate fluxes at considerably lower pressures and flow rates. Obtained variations of the oil concentrations in the permeate during volumetric concentration of the feed indicate different membrane fouling mechanisms. While the polymeric membrane showed expected oil rejection variation consistent with surface layer formation, the oil rejection of the ceramic membrane was not at the satisfactory level due to initial oil penetration to the permeate. Operation at optimal operation conditions is also essential, especially in the case of the ceramic membrane which showed relatively high oil penetration at lower cross-flow velocities and higher TMPs.

The results showed that the choice between a ceramic and a polymeric membrane for the particular application depends on better understanding of interactions between membrane material and oil droplets. Further investigation will show if the poor initial oil rejection of the ceramic membrane can be reduced without losing its advantages over the polymeric membrane.

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