

## Separation of Hydridocarbonyltris(triphenylphosphine) Rhodium (I) Catalyst Using Solvent Resistant Nanofiltration Membrane

(Pemisahan Pemangkin Rodium (I) Hidridokarboniltris(trifenilfosfin)

Menggunakan Membran Nanoturasan Tahan Pelarut)

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### ABSTRACT

An investigation was conducted into the nanofiltration of rhodium tris(triphenyl-phosphine)  $[HRh(CO)(PPh_3)_3]$  catalyst used in the hydroformylation of olefins. The large size of the catalyst ( $>400$  Da) – relative to other components of the reaction provides the opportunity for a membrane separation based on retention of the catalyst species while permeating the solvent. The compatibility of the solvent-polyimide membrane (STARMEM™ 122 and STARMEM™ 240) combinations was assessed in terms of the membrane stability in solvent plus non-zero solvent flux at 2.0 MPa. The morphology of the membrane was studied by field emission scanning electron microscopy (FESEM). The solvent flux and membrane rejection of  $HRh(CO)(PPh_3)_3$  was then determined for the catalyst-solvent-membrane combination in a dead-end pressure cell. Good  $HRh(CO)(PPh_3)_3$  rejection ( $>0.93$ ) coupled with good solvent fluxes ( $>72$  L/m<sup>2</sup>h' at 2.0 MPa) were obtained in one of the systems tested. The effect of pressure and catalyst concentration on the solvent flux and catalyst rejection was conducted. Increasing pressure substantially improved both solvent flux and catalyst rejection, while increasing catalyst concentration was found to be beneficial in terms of substantial increases in catalyst rejection without significantly affecting the solvent flux.

**Keywords:** Catalyst recycle; hydroformylation; membrane separation; solvent resistant nanofiltration

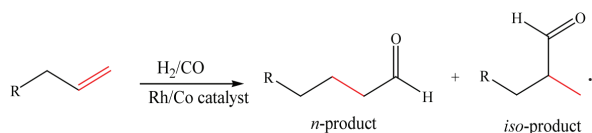
### ABSTRAK

Penyelidikan telah dijalankan ke atas teknik nanoturasan kepada pemangkin rodium tris(trifenilfosfin)  $[HRh(CO)(PPh_3)_3]$  yang digunakan dalam proses penghidroformilan olefin. Saiz pemangkin yang besar ( $>400$  Da) – berbanding dengan komponen lain dalam tindak balas memberi ruang kepada penggunaan membran yang berasaskan kepada penggunaan spesies pemangkin di samping peresapan pelarut. Keserasian pelarut-membran polimida (STARMEM™122 dan STARMEM™240) telah dinilai daripada segi kestabilan membran di dalam pelarut, berserta nilai fluks pelarut bukan sifar pada 2.0 MPa. Peresapan fluks dan pengekalan pemangkin  $HRh(CO)(PPh_3)_3$  menggunakan membran polyimide, telah dikaji untuk melihat kombinasi pemangkin-pelarut-membran di dalam sel tekanan tinggi. Pengekalan pemangkin  $[HRh(CO)(PPh_3)_3]$  yang baik ( $>0.93$ ) di samping peresapan fluks pelarut yang baik ( $>72$  L/m<sup>2</sup>h') diperolehi daripada salah satu sistem yang dikaji. Kesan daripada tekanan dan kepekatan pemangkin terhadap fluks pelarut dan pengekalan pemangkin telah dijalankan. Peningkatan tekanan yang ketara dapat menambah baik peresapan fluks pelarut dan juga pemangkin. Manakala peningkatan kepekatan pemangkin dapat meningkatkan pengekalan pemangkin tanpa mempengaruhi peresapan fluks pelarut.

**Kata kunci:** Hidroformilasi; kitar semula pemangkin; nanoturasan tahan pelarut; pemisahan menggunakan membran

### INTRODUCTION

For some industrial processes, the economic problem of catalyst separation has been eclipsed by the benefits of homogeneous catalysts could offer. One such process is the rhodium-catalyzed hydroformylation of alkenes, which provides the benefits of mild reaction conditions, high efficiencies and high yields. The overall reaction can be represented by:



The  $HRh(CO)(PPh_3)_3$  catalyst is the predominant catalyst used commercially (Cornils & Herrmann 2002) and in the presence of excess triphenylphosphine ( $PPh_3$ ) ligand gives high yields of linear versus branched aldehyde products. A majority of commercial hydroformylation processes use distillation as the primary means for catalyst recovery. This requires the use of a reaction solvent that has a higher boiling point than the aldehyde product so the dissolved, nonvolatile catalyst and solvent can be recovered in the column bottoms. Although distillation is feasible for lower molecular weight aldehydes, the separation of aldehydes with carbon numbers greater than C6 poses great difficulties (Garton et al. 2003).

Alternatives to distillation as the catalyst recovery step have been proposed using a novel solvent system that itself reversibly changes from biphasic to monophasic as a function of temperature and known as a temperature-depending multicomponent solvent (TMS) system. This concept combines the advantages of a reaction in a single phase system with the advantages of the catalyst recycling of a two-phase system (Behr et al. 2005; Shaharun et al. 2009). Another attractive feature of the hydroformylation reaction is that it is particularly well suited for a membrane separation because of the use of hydrogen and carbon monoxide (syngas) at high pressures (12–50 bar). The pressure of the syngas can act as the driving force for membrane permeation. For this and the above reasons, hydroformylation is a reaction that membrane catalyst recovery can expand and at the same time, fit well into the existing framework of the commercial reaction. In the above context, the specific objectives of this work were to study the morphology and stability of polyimide membranes, STARMEM™ 122 and STARMEM™ 240 in ethyl acetate (EA) and toluene and experimentally determine the effects of catalyst concentrations and pressure on the rejection of  $\text{HRhCO}(\text{PPh}_3)_3$  catalyst and solvent flux at 25°C.

#### MATERIALS AND METHODS

$\text{HRh}(\text{CO})(\text{PPh}_3)_3$  catalyst (98% pure) was purchased from ABCR, Germany. Two solvents were chosen in this experiment, namely toluene and EA. EA and toluene purchased from Merck, were of purity 98–99%. Nitrogen gas was supplied by MOX, with a purity of 99.99%. The STARMEM™ range of integral asymmetric membranes with active surfaces manufactured from polyimides were purchased from Membrane Extraction Technology (MET), UK. The membranes are hydrophobic and an active skin layer less than 0.2 mm in thickness with pore sizes of <50 Å covers the polyimide membrane body (Luthra et al. 2002). STARMEM™ 122 has a molecular weight cut-off (MWCO) of 220 Da and STARMEM™ 240 a MWCO of 400 Da (Machado et al. 1999). Since the molecular weight of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  catalyst is 918.79 g/mol, the active catalyst will retain because of its size. The solvent EA and toluene, on the other hand will pass through the membrane. It is important to keep in mind that the given MWCO was determined by the manufacturer under certain conditions. Different solvents and solutes have different interactions with the membrane polymer and can lead to a significantly differing MWCO. To assess a specific separation problem the membrane needs to be tested in the original solvent system.

Physical stability of the membranes was assessed by inspection of membrane disks after soaking in solvent for 24 h at 25°C. An exposure time of 24 h was selected because no visual damage could be observed after this period in preliminary experiments with each of the solvents. Field emission scanning electron microscopy (FESEM, Model: JEOL 6340) was carried out to study the cross section of the

membranes before and after the physical stability test. The membrane-solvent combination was judged incompatible if zero flux was obtained at pressure of 2.0 MPa.

The first step involved conditioning of the membrane. A membrane disc of 90 mm in diameter was cut from a membrane sheet using a Stanley knife and a steel template and then rinsed thoroughly by immersion in pure solvent (toluene or EA) overnight to remove the preserving solution. The disk was fixed in the cell, with its active surface facing the solvent, sandwiched between a viton o-ring and a porous stainless steel disk. This gave an active membrane surface area of 54.0 cm<sup>2</sup>. A teflon magnetic stirrer bar, supplied as part of the cell, was placed inside the cell, before 200 mL of solvent was poured into the cell. It was then activated by flushing it with the solvent at 20 bar for 60–80 min. To prevent performance loss, conditioned membranes were kept soaked in the solvent at room temperature. All permeation tests were carried out at room temperature which varied between 23 and 25°C.

Membrane fluxes with toluene and EA were determined first, followed by experiments to determine fluxes in the presence of catalysts. All solvent flux values quoted in this study were obtained in the following way. The cell was charged with 200 mL of the solvent and the desired pressure, 2.0 MPa applied. The volume of permeate was measured with a measuring cylinder which was capped to avoid solvent losses by evaporation. The time,  $t$ , taken for 10 mL of permeate,  $V_p$ , to be collected was recorded using a millisecond-accurate stopwatch. Solvent fluxes,  $J_s$ , were then calculated from the equation:

$$J_s = \frac{V_p}{A_m t}, \quad (1)$$

where  $A_m$  is the active membrane surface area (cm<sup>2</sup>). The permeation was stopped when flux reached a constant value.

For experiments used to determine catalyst rejection, the catalyst solution was stirred with a teflon-coated magnetic stir bar at 600 rpm to avoid concentration polarization. The experiment was stopped when half the volume of the feed solution had permeated the membrane. Retentate and permeate samples were collected in cooled flasks as a function of time, weighed and analyzed on a Shimadzu UV-VIS 3150 spectrophotometer. The rejection of catalyst was calculated from equation:

$$R = 1 - \frac{C_p}{C_r}, \quad (2)$$

where  $C_p$  and  $C_r$  is the catalyst concentration in the permeate and the retentate, respectively. Experimental runs to study the effect of pressure and initial catalyst concentration were conducted at five different pressure (0.5, 1.0, 1.5, 2.0 and 2.5 MPa) and catalyst concentration varying from 0.2 to 1.3 mM. All measurements were based on at least three samples and the average values were taken. The standard deviation on the measurements is about 5%. For all experiments, a mass balance was calculated as,

$$MB = \left( \frac{C_p V_p + C_r V_r}{C_b V_b} \right) \times 100, \quad (3)$$

where  $V_p$ ,  $V_r$ ,  $V_b$  are volumes of permeate, retentate and the bulk solution, respectively. The mass balance was found to be between 88 and 102%.

Concentrations of the retentate and permeate were determined using Shimadzu UV-VIS 3150 spectrophotometer in the visible region. The wavelengths of maximum absorbance ( $\lambda_{\max}$ ) for the HRh(CO)(PPh)<sub>3</sub> catalyst is 361 nm. Blank wavelength scans with pure solvent, toluene and EA were performed first to assure that it did not exhibit extraneous impurity peaks in the spectral region of interest and that there were no compatibility problems with the polystyrene cuvettes. The exposure of the cuvettes to toluene and EA for 8 h did not affect the wavelength scans.

## RESULTS AND DISCUSSION

Observation of membranes soaked in solvents for a period of time can give preliminary insight into the membrane stability and durability. STARMEM™ membranes curled in EA after 24 h indicating poor solvent affinity. The swelling of one surface and shrinking of the other surface leads to

a membrane curling and rolling up, which can result in unexpectedly high or low fluxes (Yang et al. 2001).

On the other hand, no changes to the active surface of the membrane were observed when the membranes were exposed to toluene. Figure 1 is the scanning electron micrographs of membrane cross-section before (a), (b) and after soaking in EA and toluene (c), (d), (e) and (f). The most significant morphological change is the increase in macrovoid formation and disintegration of the active layer when the STARMEM™ 122 membrane was soaked in EA and toluene. Macrovoids could result in compaction or collapse of membranes and therefore leading to a decrease permeate flux. The FESEM results correlated well with the observed solvent flux shown in Table 1. The STARMEM™ 220 membrane flux rate is lower compared with STARMEM™ 240. On the other hand the support layer of STARMEM™ 240 disintegrated when the membrane was soaked in EA and toluene.

As expected, the STARMEM™ 220 membrane flux rate is lower compared with STARMEM™ 240 due to the smaller MWCO. The EA fluxes are clearly higher as compared with toluene (Table 1). This may be due to the different interactions between the solvents and the membrane, lower kinematic viscosity,  $\nu$ , and air-liquid surface tension,  $\gamma$ , of EA and disintegration of the membrane active layer. No predictable effect of solvent molar volume,  $\nu_s$ , was observed.

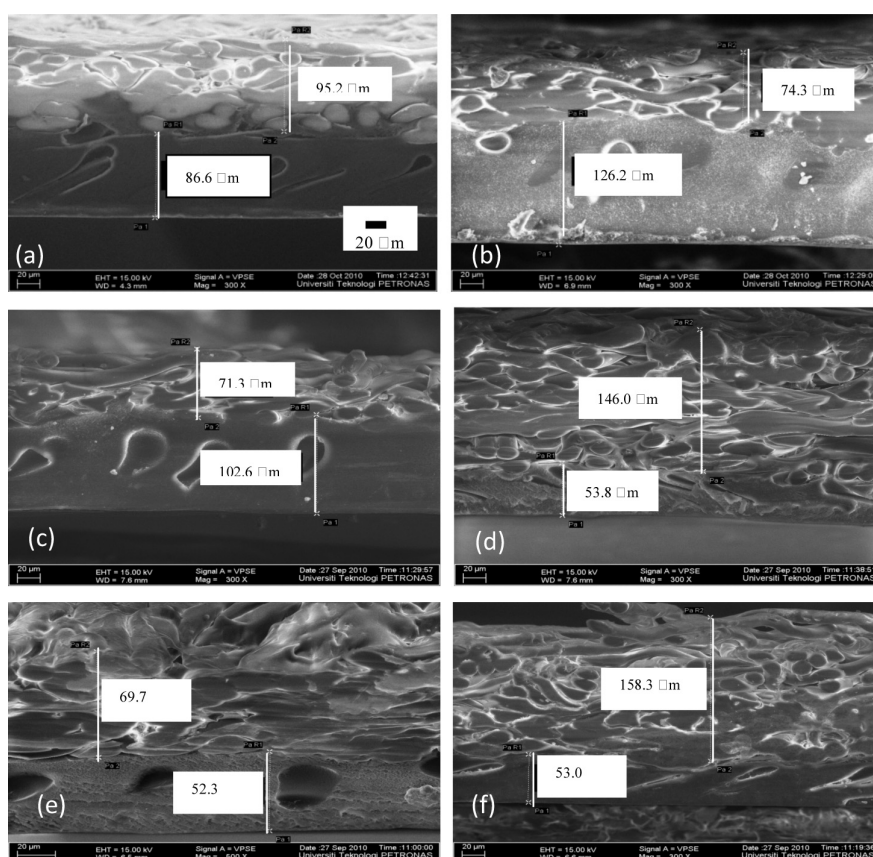


FIGURE 1. FESEM images of the cross section of STARMEM™ membrane: (a) STARMEM™ 122 (b) STARMEM™ 240 (c) STARMEM™ 122-EA, (d) STARMEM™ 240-EA, (e) STARMEM™ 122-toluene and (f) STARMEM™ 240-toluene

TABLE 1. The rejection of the 1.0 mM HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> catalyst and solvent flux obtained using the STARMEM™ membranes at 25°C with selected solvent properties ( $\nu$  and  $\gamma$  obtained from Yang et al. (2001);  $\nu_s$  was calculated from molecular mass and density)

Membrane	Solvent	$\Delta P$ (MPa)	$J_s$ (Lm <sup>2</sup> h <sup>-1</sup> )	$R$	$\nu$ (cP)	$\gamma$ (mNm <sup>-1</sup> )	$\nu_s$ (cm <sup>3</sup> mol <sup>-1</sup> )
STARMEM™ 122	toluene	2.0	23.0	0.810	0.590	27.90	106.3
STARMEM™ 122	EA	2.0	83.4	0.745	0.423	23.90	110.8
STARMEM™ 240	toluene	2.0	62.0	0.950	0.590	27.90	106.3
STARMEM™ 240	EA	2.0	94.0	0.810	0.423	23.90	110.8

Membrane swelling or contraction, sorption of molecules and liquid phase membrane phase partition coefficients of a transporting component are also likely to be important in determining membrane-solvent compatibility.

The rejection of the catalyst at 25°C using the STARMEM™ membrane-toluene and STARMEM™ membrane-EA combinations can be found in Table 1. The STARMEM™ membrane gave reasonably good HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> catalyst separation in toluene compared with EA. Formation of macrovoid and disintegration of the active layer when the STARMEM™ 122 membrane was soaked in EA and toluene may contribute to the lower catalyst rejection compared with STARMEM™ 240. It is also interesting to note the contradiction of trends between rejection of the catalyst by STARMEM™ membrane in the two solvents and the level of flux obtained. This may be due to the membrane matrix shrinkage (decreased pore size) or swelling (increased pore size). Since the rejection of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> catalyst using

STARMEM™ 122-EA system is low, further studies on the effect of pressure and catalyst concentration on the solvent flux and catalyst rejection were not carried out using the aforementioned system.

Increasing pressure was found to be beneficial in terms of both solvent flux and catalyst rejection. The results in Figure 2 shows the flux of solvent,  $J_s$ , increased linearly with transmembrane pressure,  $\Delta P$ , across the range of pressure investigated, according to the commonly observed relationship:

$$J_s = B(\Delta P - \Delta \Pi), \quad (4)$$

where  $\Delta \Pi$  is the transmembrane osmotic pressure and  $B$  is a constant. The zero intercepts reflect the fact that  $\Delta \Pi$  is negligible for single solvent systems. The comparisons of solvent fluxes obtained with and without catalyst at 25°C in Figure 2 shows that the catalyst had no significant effect

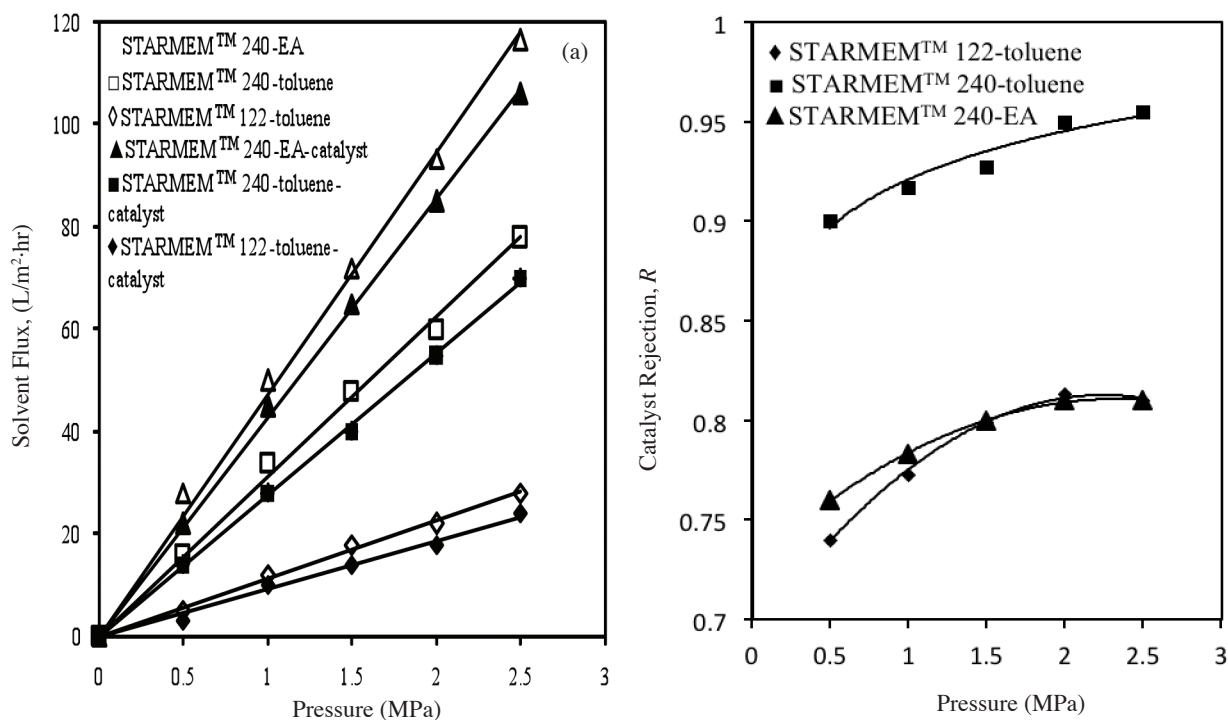


FIGURE 2. (a) The effect of pressure on solvent flux with and without catalyst and (b) the effect of pressure on catalyst rejection. Conditions: Catalyst concentration,  $C_0 = 1.0$  mM;  $T = 25^\circ\text{C}$ ; stirring speed = 600 rpm

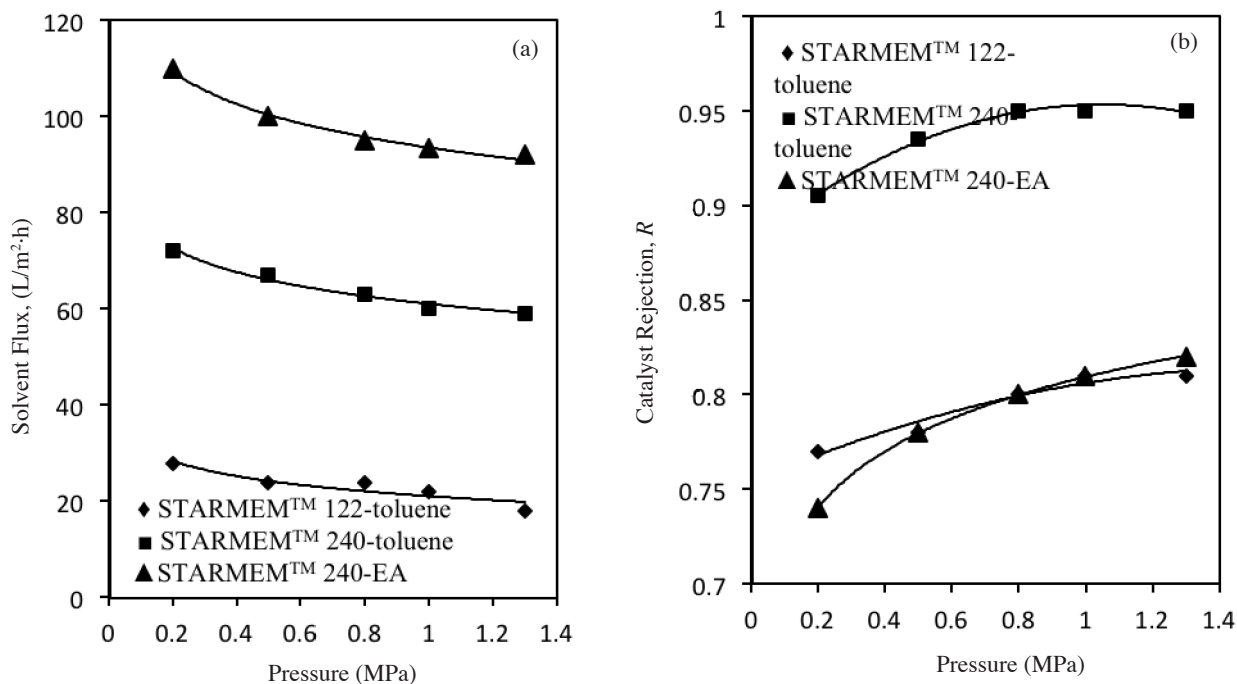


FIGURE 3. (a) The effect of catalyst concentration on solvent flux and (b) catalyst rejection. Conditions:  $P = 2.0$  MPa;  $T = 25^{\circ}\text{C}$ ; stirring speed = 600 rpm

on solvent flux under these conditions. Across the pressure range of 1.0–2.5 MPa, the catalyst rejection increases with increasing transmembrane pressure. The fact that an increase in pressure results in increased rejection is consistent with the results of Whu et al. (2000), for the SRNF of dyes from methanol. The phenomenon is due to a partially reversible, increasing compression of the active layer when the membrane is subjected to increasingly higher pressures, resulting in a tightening or sealing of the pores and a consequently better catalyst separation. In addition, fouling of the membrane may occur more rapidly at higher pressures due to the higher flow rates.

Increasing catalyst concentration,  $C_0$  was found to have contrasting effects on flux and rejection. The results in Figure 3 shows that flux decreased with increasing catalyst concentration, whilst catalyst rejection improved for STARMEM™ 240 only. The effect of catalyst concentration on rejection was very substantial and increasing concentration,  $C_0$  from 0.2 to 1.3 mM improved catalyst separation performance,  $R$  from 0.905 to 0.95 using STARMEM 240-HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>-toluene system. Whilst increasing  $C_0$  yields substantial improvements in catalyst separation, the penalty in terms of flux reduction is moderate which is 18%. The dependencies of flux and rejection on catalyst concentration observed during this study are consistent with previously published data (Scarpello et al. 2002; Whu et al. 2000). Increasing surface and pore fouling with increasing catalyst concentration may contribute to the decreasing of solvent fluxes and increasing rejections. The fact that the experiments were performed in random order indicates that any fouling is at least partially reversible.

## CONCLUSION

Asymmetric STARMEM 122 and STARMEM 240 membranes were tested in EA and toluene to evaluate membrane performances. Good catalyst rejection ( $>0.93$ ) coupled with satisfactory solvent fluxes ( $>40$  L/m<sup>2</sup>·h<sup>1</sup> at 2.0 MPa) were obtained in the STARMEM 240-HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>-toluene system. Both solvent flux and catalyst rejection were affected by variations in operating conditions of pressure and catalyst concentration. Increasing pressure was found to be beneficial in terms of both flux and catalyst rejection. Increasing catalyst concentration resulted in significantly improved catalyst separation, with only a small decline in flux.

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