

Effect of Take-up Speed on the Fabrication of Cellulose Acetate Hollow Fibre Membrane in CO₂ Separation from N₂ and CH₄

M. Mubashir, Y. F. Yeong*, T. L. Chew & K. K. Lau

Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak, Malaysia

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ABSTRACT

Over the past decades, hollow fibre membranes (HFMs) have attracted much interest of the researchers due to their extensive industrial usage in CO₂ separation processes. In the current study, we have reported the effect of take-up speed on the fabrication of cellulose acetate (CA) HFMs in gas separation. The morphology of the resultant HFMs was examined by using field emission scanning electron microscopy (FESEM). The gas permeation results obtained in this work revealed that, when take-up speed increased from free fall to 12.2 m/min, CO₂, N₂ and CH₄ permeances of the resultant CA HFM were reduced 55.68%, 87.25% and 82.00%, respectively. Meanwhile, gas pair selectivities were increased 146.18% and 247.76% respectively. These results were mainly due to the increment of polymer orientation and chain packing which suppressed the macro-voids in the HFMs and thus, the gas pair selectivities were improved. Furthermore, it was found that CA HFM spun at take-up speed of 12.2 m/min showed highest CO₂/CH₄ and CO₂/N₂ ideal selectivities of 3.9 and 3.6, respectively.

Keywords: Cellulose acetate, hollow fibre, take-up speed, CO₂ separation

1.0 INTRODUCTION

In recent years, membrane technology is considered as energy-efficient for CO₂ separation processes compared to conventional separation technologies [1]. Usually, membranes have been fabricated in four different configurations including, flat sheet, spiral wound, envelope and hollow fibre module [2]. From an industrial perspective, hollow fibre membranes (HFMs) offer advantages such as large surface area, low pressure drop, high pressure stability, high separation performance and easy scale-up [3-6]. The successful applications of polymeric HFMs in gas separation because of their substantial advantages including, low cost, higher surface area, higher mechanical strength and easy to integrate into the large-scale modules formation [7, 8].

Among the various types of polymers, cellulose acetate (CA) possesses few advantages including low cost and high chain mobility [9]. Seo and his co-workers [10] studied the gases permeation performance of CA-HFM. They found that the gas pair selectivities of CA-HFM were obtained about from 0.9 and 1.4, respectively. Subsequently, Xuehong *et al.* [11] reported the effect of air gap distance on the performance of CA HFM. They successfully eliminated the macro-voids from CA-HFM spun at the air gap distance of 2.5 cm, which contributed to the increment of CO₂/CH₄ gas pair selectivity from 2.8 to 3.3.

On the other hand, as reported in the literature, fabrication of HFMs is complex and their gases permeation performance depends on the spinning parameters. Spinning parameters including, spinning temperature, dope

* Corresponding to: Y. F. Yeong (email: yinfong.yeong@utp.edu.my)

composition, dope flow rate, take-up speed and air-gap distance facilitate the phase stability, phase separation and spongy morphology in the membrane. Therefore, these factors have tendency to reduce non-selective voids of HFMs and thus, improves the gas separation performance [12, 13]. However, take-up speed is considered as a significant spinning condition which can enhance the gases permeation performance of HFMs [14].

In 2012, Kapantaidakis and his co-workers [14] reported the influence of take-up speed on the permeation performance of PES/PI HFM in CO₂ separation from N₂. CO₂/N₂ ideal selectivity was increased from 50 to 59 on the increment of take-up speed from 5 m/min to 12.5 m/min. Subsequently, Yong *et al.* [15] varied the take-up speed from 6 m/min to 12.5 m/min over PIM-1 HFM. They improved the gas pair selectivities of 22.7% and 86.5%, respectively, compared to those values obtained over PIM-1 HFM fabricated at a take-up speed of 6 m/min.

A similar observation has also been reported by Askari *et al.* [16] over 6FDA-durene HFM in CO₂/CH₄ separation. They found that when the take-up speed varied from 4 m/min to 12 m/min, the CO₂ permeance dropped 60.7%, while CO₂/CH₄ ideal selectivity of the membrane increased by 98.8%. These results were mainly attributed to the increment of take-up speed which increased the polymer chain packing [17]. The increment in polymer chain packing suppressed the macro-voids in the HFMs and thus, CO₂/CH₄ separation performance increased [18]. On the basis of above considerations, the effect of take-up speed on the fabrication of CA-HFM in CO₂ separation is scarcely reported in the literature. Thus, in the current work, we reported the effect of take-up speed on the formation of CA-HFM in CO₂ separation from N₂ and CH₄.

Subsequently, the morphology of HFMs is characterized by using FESEM. In addition, the permeation performance of the HFMs in CO₂ separation from N₂ and CH₄ is evaluated.

2.0 METHODS

2.1 Materials

Cellulose acetate (Mn ~ 30,000) was supplied from Sigma Aldrich (Malaysia). N-methyl-pyrrolidone (NMP, 99.80%) and n-Hexane (> 99.99%) solvents were purchased from Merck (Malaysia). The polymer and solvents were used as received.

2.2 Preparation of Dope Solution

Firstly, CA powder was dried in a vacuum oven. Then, 18 wt% of CA/NMP solution was prepared using a similar procedure as described elsewhere [18]. After that, the dope solution was poured into the reservoir and allowed to degas at room temperature for overnight.

2.3 Fibre Spinning

In the present work, dry-wet phase inversion method was adopted using single layer spinneret to fabricate the HFMs as described elsewhere [4]. Firstly, NMP/water (90%/10%) solution was prepared as bore fluid. Then, the bore fluid was extruded at 0.9 ml/min through the spinneret using ISCO syringe pump. In the next step, dope solution was pumped at 3.0 ml/min to the spinneret under N₂ atmosphere. After that, nascent fibre was spun and it passed through the coagulant bath. Then, the fibre was collected through a take-up roller. During the spinning process, the air gap distance was kept constant at 2.5 cm

Table 1 Spinning conditions of CA HFM fabricate in the present work

Parameters	Condition
Dope solution	CA/NMP
Bore fluid (NMP/water, wt %)	90/10
Spinneret dimensions (OD/ID, mm)	0.8/0.4
Dope flow rate (ml/min)	3.0
Bore flow rate (ml/min)	0.9
Air gap distance (cm)	2.5
Coagulant temperature (°C)	25

while take-up speed was varied from free fall (3.2 m/min) to 12.2 m/min. The spinning experiment was conducted at room temperature and Table 1 summarizes the spinning conditions of CA HFM fabricated in present work.

2.4 Solvent Exchange

NMP solvent was removed from the fibres using tap water, methanol and n-hexane. Firstly, fibres were rapidly immersed in the water for 3 days and it was changed after every 8h. Subsequently, 3 times solvent exchange was conducted using methanol for 30 min under the continuous stirring. In the next step, solvent exchange of fibres with n-hexane was repeated for 30 min under the continuous stirring, for 3 times. Lastly, all fibres were preceded for drying at ambient temperature before characterization and permeation tests [12].

2.5 Characterization

2.5.1 Field Emission Scanning Electron Microscope (FESEM)

In order to investigate the morphology of CA-HFMs, field emission scanning electron microscope (FESEM, Zeiss Supra 55 VP) was used. FESEM was operated with electronic beam energy of 5 kV and images at different magnifications were produced.

2.6 Gas Permeation Study

Firstly, HFMs were packed together in a 12 cm long module using epoxy resin. After that, the module was purged at least three times using N₂. Then, permeation test was carried out at room temperature with operating feed pressure of 3 bar. In the next step, feed gases were circulated at the shell side of the module with the predetermined flow rates of 200 ml/min. After that, the system was allowed to stabilize for 30 min and thus, the data points were collected for at least 15 min. The flow rate of permeate gas was measured from the tube side of the fibres using bubble flow meter. Then, CO₂ permeance was calculated using equation (1) as follows [19]:

$$\frac{P_{CO_2}}{L} = \frac{Q}{A \Delta P} = \frac{Q}{n \pi D L_m \Delta P} \quad (1)$$

where Q , n , D , L_m and ΔP is permeate flow rate, number of fibres, outer diameter of fibre, effective length and pressure drop, respectively. P_{CO_2} is the permeance of CO₂ of CA HFMs with units of GPU. Meanwhile, CO₂ and CH₄ permeances of HFM were divided in order to calculate the CO₂/CH₄ ideal selectivity using equation (2) as follows [19]:

$$a_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \quad (2)$$

The same procedure was repeated in order to determine CO₂ permeance and CO₂/N₂ selectivity of HFMs.

3.0 RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 Field Emission Scanning Electron Microscopy (FESEM)

FESEM images of cross-sectional view of CA-HFMs spun at different take-up speed are presented in Figure 1. Referring to Figure 1, it can be observed that increment in take-up speed from free fall (3.2 m/min) to 12.2 m/min resulted to suppressed the macro-voids on the cross-section of CA-HFM are suppressed. Subsequently, the diameter and wall thickness of the CA HFM were also decreased from 210.71 μm to 100.5 μm and 50.92 μm to 23.63 μm , respectively. These results are mainly attributed to the increase in polymer chain packing along with the increment of take-up speed [17]. When the take-up speed increases, extensional stress increases and thus, induced the chain packing which retards the penetration of external coagulant [18]. Furthermore, the increment in extensional stress also contributes to shrink the fibre dimensions and forced the internal solvent to flow outside radially which inhibits the diffusion of external coagulant [20]. Therefore, macro-voids, diameter and wall thickness were reduced with the increment of take-up speed.

3.2 Gas Permeation Study and Comparison with the Literature Results

Figure 2 illustrates the typical effect of take-up speed on the single gas permeation performance of CA-HFMs in gas separation. The data were

reproduced with an error of $\pm 3\%$. Referring to Figure 2, it is observed that CO₂, N₂ and CH₄ permeances decreased dramatically with the increment of take-up speed from free fall to 12.2 m/min. The reduction in gases permeance was expected due to the decrease in number macro-voids and increase in polymer chain packing of HFM [18]. Therefore, characteristics of the active skin layer improved and thus, gas pair selectivities were increased [19]. Furthermore, the increment in take-up speed induced the extensional stress on the fibres which decreased the Knudsen pores in HFMs [20]. In addition, viscous drag force also came into the account on the increment of take-up speed and it contributed to reduce the non-selective voids of the HFMs [21-23]. Therefore, CO₂, N₂ and CH₄ permeances of CA HFM were reduced 55.68%, 87.25% and 82.00%, respectively, compared to those results obtained for CA HFM spun at free fall.

Besides, from Figure 2, it has been found that CO₂/CH₄ and CO₂/N₂ ideal selectivities were increased from 1.6 to 3.9 and 1.0 to 3.6, respectively, with the increment in take-up speed. This result could be because of greater reduction in N₂ and CH₄ permeance compared to the CO₂ permeance. Greater reduction in N₂ and CH₄ permeance was the result of reduction in Knudsen pores in CA HFMs [20]. Therefore, CO₂/CH₄ and CO₂/N₂ ideal selectivities were increased 146.18% and 247.76%, respectively, compared to those values obtained for CA HFM spun at free fall.

Consequently, the comparison between separation performance of CA-HFMs fabricated in the present work and other CA based HFMs from literature is shown in Table 2. From Table 2, HFMs fabricated in this work

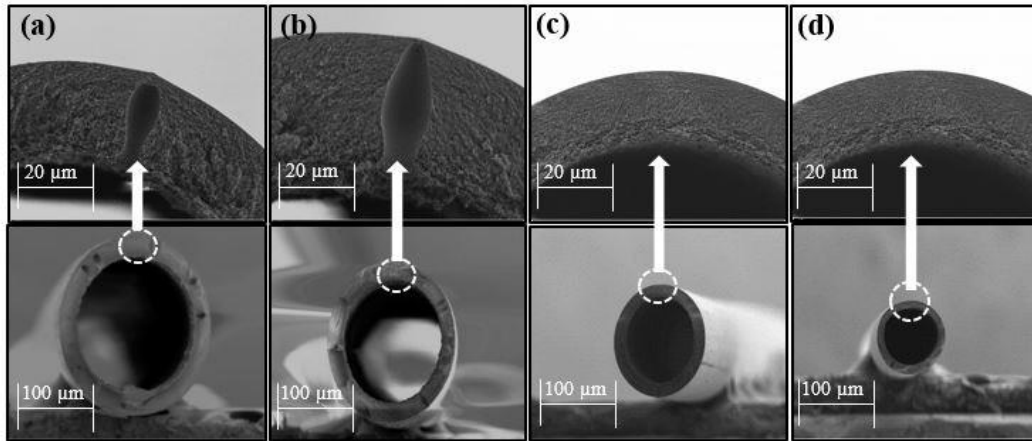


Figure 1 FESEM images of cross-sectional view of CA HFM at various take up speed; (a) free fall, (b) 4.2 m/min, (c) 8.2 m/min, (d) 12.2 m/min

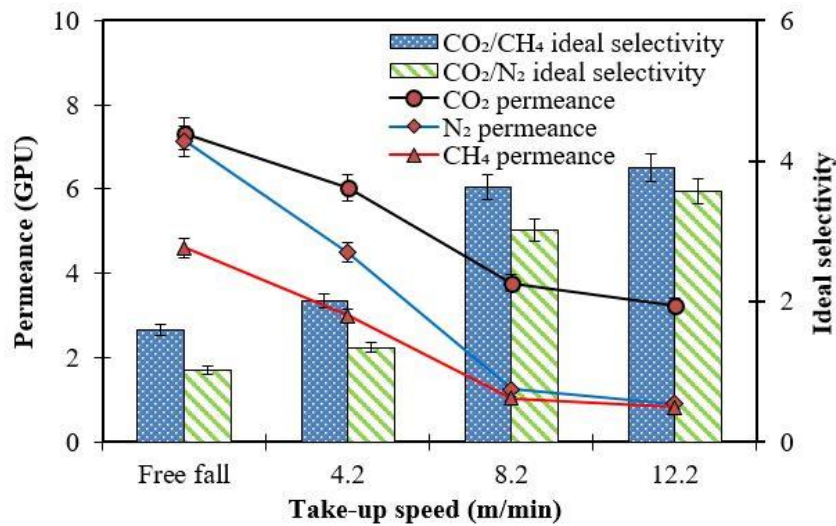


Figure 2 Typical effect of take-up speed on the single gas permeation performance of CA-HFMs in gas separation

Table 2 Comparison of CO₂/CH₄ and CO₂/N₂ ideal selectivities of CA HFM fabricated in the present work with reported literature

HFM	Take-up speed (m/min)	Air gap distance (cm)	CO ₂ permeance (GPU)	N ₂ permeance (GPU)	CO ₂ /CH ₄ ideal selectivity	CO ₂ /N ₂ ideal selectivity	Ref.
CA	Free fall	2.5	7.3	7.1	1.6	1.0	This work
CA	12.2	2.5	3.2	0.9	3.9	3.6	[10]
CA	5.1	10	52.0	38.6	0.9	1.3	[10]
CA	5.1	15	33.9	23.6	0.9	1.4	[10]
CA	Free fall	0.0	NA	3.3	NA	NA	[24]

showed superior gas pair selectivities compared to the other CA based HFMs [10]. This result could be due to the

effect of take-up speed which decreases the macro-voids and increases polymer chain packing of HFMs and thus, higher

permeation performance of CA-HFMs was achieved [10]. From the above discussion, it can be concluded that take-up speed of 12.2 m/min showed the highest gas pair selectivities.

4.0 CONCLUSION

In this study, CA HFM was fabricated for CO₂ separation. Subsequently, it has been characterized by using FESEM. The gas permeation results obtained in this work revealed that CO₂, N₂ and CH₄ permeances of CA HFM were reduced about 55.68%, 87.25% and 82.00% respectively, while, gas pair selectivities were increased about 146.18% and 247.76% respectively, with the increment of take-up speed. These results were mainly due to the polymer orientation and packing which suppressed the macro-voids in the HFMs. Furthermore, it can be concluded that take-up speed of 12.2 m/min is an optimum speed for fabrication of CA HFM.

5.0 RECOMMENDATIONS

On the basis of experimental studies, it was found that CA-HFM possesses lower CO₂/CH₄ and CO₂/N₂ ideal selectivities. Therefore, intensive studies on post-treatment of CA-HFM should be conducted in order to enhance its performance in gas separation. Subsequently, metal organic framework (MOFs), covalent organic framework (COFs), covalent organic polymers (COPs) and metal-organic polyhedra (MOPs) can be considered as potential particles to be incorporated into CA matrix to enhance membrane selectivity. Furthermore, the effect of spinneret temperature, dope composition and spinning bath length should be studied for the possible

improvement of the membrane performance in gas separation.

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