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#### Effect of air-gap length on Carbon dioxide stripping performance of 1 surface modified Polysulfone hollow fiber membrane contactor 2 3 M. Rahbari-Sisakht<sup>a,b</sup>, F. Korminouri<sup>a</sup>, D. Emadzadeh<sup>a,b</sup>, T. Matsuura<sup>c</sup> and 4 A.F. Ismail<sup>a</sup>,\* 5 6 <sup>a</sup> Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia (UTM), 81310 Skudai, Johor, 7 Malaysia 8 <sup>b</sup> Department of Chemical Engineering, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran 9 <sup>c</sup> Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur St., Ontario K1N 6N5, Canada 10 11 \*Corresponding author: Tel.: +60 75535592; Fax: +60 75535925. E-mail addresses: afauzi@utm.my and 12 fauzi.ismail@gmail.com. 13 14 ABSTRACT 15

Surface Modifying Macromolecule (SMM) blended PSf hollow fibers were spun at different air-16 gaps to evaluate CO<sub>2</sub> stripping from aqueous DEA solution and water. The fabricated membranes 17 were firstly subjected to different characterization methods such as contact angle and liquid entry 18 19 pressure measurement to evaluate the membrane's hydrophobicity and wetting resistance, 20 respectively. To determine pore size and effective porosity of the membranes, the pure helium permeation test was performed. Morphological study of the membranes was conducted by 21 scanning electron microscopy (SEM) and atomic force microscopy (AFM). CO<sub>2</sub> stripping test 22 was carried out to investigate the effects of operating variables such as liquid and gas velocity. 23 temperature and DEA concentration on CO<sub>2</sub> stripping flux. It was found that the increase of 24 liquid velocity resulted in enhanced CO<sub>2</sub> stripping flux. On the other hand, the increase in gas 25 velocity did not exert significant influence on the stripping flux. The increase in temperature and 26 DEA concentration both enhanced the stripping flux. Lastly, it was concluded that the hollow 27 fiber spun in this work at 15 cm air-gap could achieve the best stripping flux among all the 28 29 membranes fabricated so far for the CO<sub>2</sub> stripping.

Keywords: Polysulfone hollow fiber membrane; CO<sub>2</sub> stripping; membrane contactor; air-gap
length.

# 33 1. Introduction

Capture and removal of carbon dioxide (CO<sub>2</sub>), the main greenhouse gas, from fossil fuel 34 35 combustion is arguably the most critical environmental concern worldwide. More than 80% of industrial and domestic energy utilization are provided by fossil fuels and contribute significantly 36 37 to escalation of atmospheric CO<sub>2</sub> levels, which results inevitably in increase of significant climate change.<sup>1</sup>A technology for CO<sub>2</sub> removal from gas flows is hence required. Several 38 39 techniques are presently applied to separate CO<sub>2</sub> from gas streams using various chemical and physical processes including absorption, adsorption, cryogenic and membranes.<sup>2-11</sup>The 40 conventional technologies for CO<sub>2</sub> capture face some operational downsides for instance, 41 flooding, foaming and weeping, which can adversely influence performance and costs of power 42 stations. Hollow fiber membrane (HFM) contactor is an energy and cost efficient technology, 43 which can be applied for depletion of  $CO_2$  from a variety of industrial process gas streams. HFM 44 contactor is a modular and flexible device with a high contact area for liquid and gas phase and 45 high mass transfer rate per unit volume. Due to the noticeable advantages of HFM contactors, in 46 recent years there is an increasing acceptance to use this technology for gas separation.<sup>12-21</sup>. The 47 major challenge of using HFs is membrane wettability which results in escalation of mass 48 transfer resistance and reduction of CO<sub>2</sub> flux. To prevent membrane wetting hydrophobic 49 polymers should be chosen. 50

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Polysulfone (PSf) has been used for a long time as a polymeric material for HFM 52 preparation. This polymer, according to Rahbari-Sisakht et al.<sup>22</sup> despite not being highly 53 54 hydrophobic can be a surpassing option for membrane fabrication due to its great thermal and mechanical endurance and high solubility in the solvents. To elevate the hydrophobicity of 55 membrane surface, blending surface modified macromolecules (SMM) in the polymer dope can 56 be a favored method. SMM is an amphipathic macromolecule consisting of hydrophilic and 57 hydrophobic parts. In a polymer blend, thermodynamic incompatibility between polymers 58 usually causes demixing of polymers to occur. If the polymer system is equilibrated in air, the 59 60 polymer with the lowest surface energy will concentrate at the air interface and reduce the

system's interfacial tension as a consequence.<sup>23</sup> In our previous work, EDX results showed that 61 during hollow fiber spinning, SMM tends to migrate to membrane – air surface and changes the 62 membrane outer surface properties.<sup>24</sup> The SMM surface migration occurs during membrane 63 fabrication process due to the difference in energy levels of the SMM and base polymer, which 64 leads to improve hydrophobicity of the HF surface. The detailed kinetics and mechanism of 65 SMM surface migration is presented in earlier study.<sup>25</sup> The air-gap is one of the principal 66 67 spinning conditions that affects the amount of migrated SMM to the membrane-interface by providing a sufficient amount of time for SMM migration. The study into the effect of air-gap on 68 membrane performance and structure has been conducted over the past few decades for various 69 separation processes.<sup>26-36</sup> 70

71

MC systems have a considerable potential to regenerate or desorb the absorbent solution. In the absorption process, unwanted gas  $(CO_2)$  is absorbed by the liquid absorbent. In the regeneration procedure, on the other hand, desorption of  $CO_2$  takes place. The liquid absorbent is in contact with one end of the HFM pore and  $CO_2$  diffuses through the pore, and stripped by the stripping gas at the other end of the pore to regenerate the liquid absorbent.

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Many studies have focused on the absorption unit using HFMcontactors,<sup>37-39</sup>while only a 78 few works have been carried out until now on CO<sub>2</sub> stripping through MCs. Recently, a research 79 has been done by Khaisri et al.<sup>40</sup> to strip CO<sub>2</sub> from monoethanolamine (MEA) solution using 80 polytetrafluoroethylene (PTFE)HFM. They concluded that the stripping efficiency was elevated 81 with the increase of the liquid velocity, operating temperature and absorbent concentration. On 82 the other hand, the gas side mass transfer resistance did not deeply affect the CO<sub>2</sub> desorption 83 flux. Kumazawa<sup>41</sup> conducted a study on CO<sub>2</sub> desorption from 2-amino-2-methyl-1-propanol 84 (AMP) through PTFE membrane. They found that desorption process is ascribed to diffusion and 85 86 chemical reaction in the liquid side. They concluded that an increase in concentration of AMP and the loaded CO<sub>2</sub> in the solution resulted in enhancement of total mass transfer coefficient. 87 Naim *et al.*<sup>42</sup> produced PVDF membrane to strip CO<sub>2</sub> from aqueous diethanolamine (DEA) 88 solution. They added LiCl in the polymer solution as an additive to investigate the effect of 89 90 different LiCl levels on stripping performance of the membrane. A linear increase in stripping flux was observed with increasing LiCl concentration. A study by Mansourizadeh and Ismai<sup>43</sup> 91

focused on CO<sub>2</sub> stripping from water using PVDF membrane. Their results showed that the 92 increase of inlet liquid concentration led to increase of CO<sub>2</sub> stripping performance. Rahbari-93 Sisakht et al.<sup>44</sup> fabricated PVDF fibers modified by SMM to strip CO<sub>2</sub> from diethanolamine 94 solution. Their experimental found that the CO<sub>2</sub> desorption flux was enhanced with increasing 95 DEA concentration, solution temperature and liquid velocity. In other works,<sup>45</sup> wet spun 96 polyetherimide (PEI) membrane blended with polyethylene glycol (PEG) was developed to 97 evaluate the effect of various PEI concentrations (13-16 wt %) on CO<sub>2</sub> stripping performance 98 from DEA solution. It was found that the membrane produced with 14 wt% PEI concentration 99 achieved the maximum CO<sub>2</sub> flux of  $2.7 \times 10^{-2}$  (mol/m<sup>2</sup>.s). 100

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Despite the above mentioned researches on stripping applications, to our knowledge, no research has been conducted thus far into the effect of SMM migration to the HF membrane surface on CO<sub>2</sub> stripping flux from aqueous DEA solution and water. The first attempt is hence made in the present work to manufacture SMM blended PSf HFs with different air-gap distances, to characterize the HFs so manufactured by various methods and to investigate the performance of CO<sub>2</sub> stripping flux from DEA and water in a MC application.

#### 108 **2.** Experimental

#### 109 2.1. HFM preparation

110 To preprare spinning dope 17 wt% PSf (Udel P-1700, from Solvay Advance Polymer) and 1 111 wt% laboratory synthisized SMM was mixed in N-methyl-2-pyrrolidone (NMP>99.5%, 112 purchased from Merck) by mechanical stirring at 60 °C to achieve a stable and uniform solution. 113 Fig. 1 shows the SMM structure, where *m* represents the repeating units of CF<sub>2</sub> and equals to 114 7.58, *y* indicates a,o-aminopropyl poly (dimethyl siloxane) (PDMS) repeating units and is equal 115 to 9.81 and *q* reveals repeating unit of urea and equals to 10.14. The detailed descriptions of 116 SMM synthesis were given in other literatures.<sup>25</sup>



118

$$F - (CF_2)_m - (CH_2)_2 - O - C - NH - (CH_2)_2 - (CH_2)_2 - (CH_2)_2 - (CH_2)_2 - (CH_2)_3 - (CH$$

119 Fig. 1: Structure of SMM

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121	Aqueous solution of diethanolamine (DEA>99%, from Merck ) was useded as the liquid
122	absorbent in MC application. The sweeping and feed gaswere pure $\mathrm{N}_2$ and $\mathrm{CO}_2\text{,}$ respectively.
123	After degassing the resulting mixture by the aid of ultrasonic water bath, the PSf HFs ( $M_1$ - $M_7$ )
124	were spun with air-gaps of 0, 5, 10, 15, 20, 30 and 50 cm, respectively, according to the method
125	described earlier. <sup>46</sup> Table 1 gives the detailed dry-wet spinning conditions applied in this work. To
126	completely remove the residue of the additive, solvent and any impurities, the spun HFswere
127	soaked in tap water for 3 days, before being dried at room temperature.

128

129	Table 1         Experimental spinning conditio	ns
	Dope extrusion rate (ml/min)	4.5
	Composition of bore fluid	NMP/water (60/40)
	Bore fluid rate (ml/min)	2.00
	Coagulation medium	Tap water
	Spinneret dimension, o.d./i.d (mm)	1.20/0.55
	Air-gap (cm)	0, 5, 10, 15, 20, 30 and 50
	Temperature of coagulant (°C)	25

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#### 131 2.2. Charecterization of prepared HFMs

PSf membranes were subjected to various charecterization methods, which meticulously 132 detailed in our previous study.<sup>44</sup> To acquire the average pore radius and the effective surface 133 porosity of theHFs,helium permeation experiment was conducted based on the method 134 describedin our earlier work.<sup>44</sup> Cotact angle (CA) of the fiber's outer dry surface was measured to 135 obtain information about surface hydrophobicity of the HFs. To determine the membrane's 136 resisitance to the wetting, liquid entry pressure for both water (LEPw) and DEA (LEP<sub>DEA</sub>) was 137 measured.<sup>44</sup> LEPsare considered as the pressure at which the first droplet of liquidwas 138 perceived on the upperskin of the HFM. HF's overall porosity ( $\varepsilon_m$ ) was obtained using 139 gravimetric method. To evaluateHF's mechanical endurance, collapsing pressure of each HF was 140 measured.<sup>44</sup> Scanning electron microscope (SEM, tabletop microscope, TM3000) was used to 141 obtain images of HF's cross-section and outer skin. Roughness  $(R_a)$  was obtained by atomic 142

force microscopy (AFM) using AFM equipment (SPA 300 HV, Japan) by the method of
Khayet*et al.*<sup>47</sup>

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# 146 **2.3.** CO<sub>2</sub> stripping evaluation

Fig. 2 indicates the experimental setup used for CO<sub>2</sub> stripping by the MC system. Thirty 147 HFs were assembled into bundles and placed in a stainless steel module which is specified in 148 details in Table 2. The aqueous DEA solution (1 DEA mol/L) or water was presaturated with 149 pure CO<sub>2</sub> up to 0.0006 mol/L, unless otherwise stated, and loaded in the feed reservoir. The CO<sub>2</sub> 150 presaturated liquid and the stripping agent (pure N<sub>2</sub>) flowed in the lumen and shell side of HFs. 151 respectively, in a counterflow mode. The calibrated flow meters were applied to regulate the 152 pressure and flow rate of the gas and liquid stream. In order to prohibit the bubble dispersion into 153 the liquid, the difference of  $0.2 \times 10^5$  bar in pressure between N<sub>2</sub> and the liquid stream was applied. 154 The inlet and outlet CO<sub>2</sub> concentration in the liquid side was determined by the titration 155 methoddescribed in details by Li and Chang.<sup>48</sup> 156

157 The flux of stripped  $CO_2$  was obtained using the equation below:

158 
$$J_{CO_2} = \frac{C_{l,i} - C_{l,o}}{A_i} \times Q_l$$
 (1)

where  $J_{CO_2}$  is the flux of CO<sub>2</sub> stripped from liquid (mol/m<sup>2</sup>.s),  $C_{l,i}$  and  $C_{l,o}$  indicate concentration of CO<sub>2</sub> (mol/m<sup>3</sup>) in the liquid streamat the module inlet and outlet, respectively.  $Q_l$  is the liquid flow rate (m<sup>3</sup>/s) and  $A_i$  is the HF inner surface (m<sup>2</sup>).<sup>49</sup>



# **3. Results and Discussion**

### 174 **3.1.** Structure of PSf membranes

The experimental findings of characterization tests are summarized in Table 3. From the table the fiber's mean pore sizei was very large at the 30 and 50 cm air-gap, which is probably ascribed to elongational effect. As well, the migration of a larger amonunt of SMM to the fiber surface may also have contributed to pore size enlargement.

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The enhancement of contact angle (CA) from 85.14±0.87° to 93.01±0.93° with increasing 180 181 air-gap up to 15 cm can be attributed to the presence of a larger amount of SMM at the HF surface.On the other hand, a trend of decline in CA from 15 to 50 cm can be attributed to the 182 increased pore size for larger air-gaps. Notably, the increase of the pore size facilitates 183 penetration of water into the HF membrane pores, resulting the redction in CA values. According 184 to the AFM analysis the roughness of HF outside surfaceincreased as the air gap increased from 185 0 to 50 cm, which may also have contributed to the enhancement of CA. Further increase in 186 roghness from the air gap of 15 to 50 cm is most likely associated with the increase in pore size, 187 which, as mentioned above has caused the desrease of CA. In any case, all HF surfaces exhibited 188 CA of higher than that of the plain dry spun PSf HF( $63\pm1.5^{\circ}$ ) by Rahbari-Sisakht *et al.*<sup>24</sup>, which is 189 another evidence of the surface migration of hydrophobic SMM. 190

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The collapsing pressure of PSf HF membranes has gradually increased as the air-gap changed from 0 to 50 cm, which was mainly caused by interaction of base polymer with surface migrated SMM.

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The HFs overall porosities are considered to behigh enough for MC due to the low polymer concentration in the spinning solution. Furthermore, surprising decrease of The overall porosity decreased gradually with the increase in the air-gap, which is associated with the reduced HF dimension (i.d, o.d and wall thickness) at the higher air-gaps. In addition, a parallel relationship is found between CA and LEPw, i.e. both CA and LEPw increased up to 15 cm airgap, decreased a little from 15 to 20 cm and then increased continuously from 20 to 50 cm. Hence, it can be concluded that LEPw was also influenced by both the pore size and the amount Page 9 of 28

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of migrated SMM to the surface. M<sub>4</sub> membrane showed the highest resistance to the wetting for 203 both water and aqueous DEA solution. 204

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Table 3

#### Experimental data of charecterization testsfor PSf HFs

HF Number	Air-gap distance (cm)	Average pore size (nm)	Effective surface porosity $\frac{\varepsilon}{L_p}(m^{-1})$	LEPw (×10 <sup>5</sup> pa)	LEP <sub>DEA</sub> (×10 <sup>5</sup> pa) at 80 °C	CA (outer surface)	Collapsin g pressure (×10 <sup>5</sup> pa)	Overall porosity (%)	Roughnes (R <sub>a</sub> )
$M_1$	0	108.95	2.00	5.00±0.72	4.5±0.25	85.14±0.87	7	70	4.12
$M_2$	5	141.18	1.97	5.00±1.32	4.5±0.68	85.81±1.46	7.5	70	4.85
$M_3$	10	88.61	3.84	$5.00 \pm 0.40$	$4.00 \pm 1.40$	87.23±1.23	8	69	5.54
$M_4$	15	21.27	33.28	5.5±0.64	5.00±0.25	93.01±0.93	8.5	68	6.41
$M_5$	20	62.96	11.40	3.5±1.07	3.00±0.50	88.80±1.37	8.5	68	7.31
$M_6$	30	257.70	3.10	4±0.82	3.50±1.25	90.00±1.07	9	66	8.06
$M_7$	50	774.83	0.34	4.5±0.53	3.50±0.50	91.78±1.29	9	58	8.58

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#### 3.2. SEM observation 212

213 Fig. 3 displaces the SEM images of the HF's cross-section and the outer skin surface for air-gaps ranging from 0 to 50 cm. The HF diameters declined from 952 to 654 µm (o.d) and 214 from 604 to 460 µm (i.d), respectively, as the air-gap changed from 0 to 50 cm due to HF 215 eleongation. All HFs have porous skin layers on both inner and outer surfaces. Finger-like voides 216 extended from both sides to the middlesection of the HF. As shown in Fig. 3 the size of the 217 macrovoids in the HF lumen side became larger as the air-gap length increased, which can be 218 ascribed to the more contact time of the spun HF with the inner coagulant. 219





NL D5.0 ×800 100 um

NL D4.4 ×10k 10 um



Fig. 3 SEM images of the PSFhollow fibers (a) cross-section, (b) outer surface.

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- 222

# 223 3.3. AFM analysis

Fig. 4 shows the 3D AFM micrographs of the HF's outer surface. The roughness of the 224 HF's  $(M_1-M_7)$  outer surface increases gradually with an increase in air-gap, as it is quantitatively 225 226 shown in Fig. 5. The similar morphological behaviour was observed for surface modified polyethersulfone (PES) membranes spunwith various air-gaps of 50 to 90 cm, which was 227 attributed to the presence of larger amount of SMM at the HF surface.<sup>50</sup> It is noteworthy that the 228 parallel nodular alignment isobvious for short air-gaps and it becomes more obscure as the air-229 230 gap increases. It is likely because of polymer relaxation that occurs while the pristine HF is traveling through the air-gap. 231







**Fig. 4** AFM 3D micrographs of the PSf hollow fibers (outer surface).







Fig. 5 Roughness parameter of HF's outer surface vs. air-gap length.

# 236 **3.4.** CO<sub>2</sub> stripping evaluation results

Fig. 6 illustrates the influence of liquid (1 mol/L, DEA) velocity on stripping flux at the liquid temperature of 80 °C. The figure shows an increasing trend in stripping flux as DEA velocity increases, which confirms the decreased resistance of liquid phase boundary layer.<sup>51</sup>A maximum stripping flux of  $4.50 \times 10^{-2}$  (mol/m<sup>2</sup>.s) was achieved by HF M<sub>4</sub> at DEA velocity of 0.7 (m/s). A similar behavior can be seen by Fig. 7 when the liquid absorbent is water.

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The membrane that has been fabricated using 15 cm air gap length  $(M_4)$  is unique in many aspects among all the studied HFs. In particular,  $M_4$  has the highest effective surface porosity (see Table 3), enabling the fastest gas transport due either to the large surface porosity or to the small effective membrane thickness. Its LEPw is also the highest due to the smallest pore size and the highest contact angle. Thus, M4 has all the desirable features of MC applications.



Liquid velocity (m/s)

Fig. 6 CO<sub>2</sub> stripping flux vs. liquid velocity (DEA solution). (T<sub>DEA</sub>=80 °C, M<sub>DEA</sub>=1 mol/L, gas
 flowrate=50 ml/min).



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**Fig. 7** CO<sub>2</sub> stripping flux vs. liquid velocity (water). (T=80  $^{\circ}$ C, gas flow rate = 50 ml/min).

In Table 4 and 5 comparisons were made between the  $CO_2$  stripping fluxes from aqueous DEA solution and water, respectively, of the membranes fabricated in this work and those reported in other studies.<sup>44,52-55</sup> The velocity of both DEA solution and water flow was maintained at 0.7 m/s. As the tables show, M<sub>4</sub> membrane fabricated in this work at 15 cm air-gap and modified with 1wt% SMM, shows the best  $CO_2$  fluxes.

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	Polymer	Air-gap		CO <sub>2</sub> flux		Liquid
Membrane	material	(cm)	Additive	(mol/m <sup>2</sup> .s)	Reference	absorbent
M <sub>1</sub>	PSf	0	1wt%SMM	2.70×10 <sup>-2</sup>	This work	DEA
$M_2$	PSf	5	1wt% SMM	1.20×10 <sup>-2</sup>	This work	DEA
M <sub>3</sub>	PSf	10	1wt% SMM	3.30×10 <sup>-2</sup>	This work	DEA
$M_4$	PSf	15	1wt% SMM	4.60×10 <sup>-2</sup>	This work	DEA
M <sub>5</sub>	PSf	20	1wt% SMM	3.90×10 <sup>-2</sup>	This work	DEA 👆
$M_6$	PSf	30	1wt% SMM	3.10×10 <sup>-2</sup>	This work	DEA 🕖
$M_7$	PSf	50	1wt% SMM	1.00×10 <sup>-2</sup>	This work	DEA 🔁
-	PVDF	5	1wt% SMM	1.20×10 <sup>-3</sup>	[44]	DEA 👧
-	PVDF	0	-	2.20×10 <sup>-2</sup>	[55]	DEA
-	PVDF	0	5wt% PEG	3.70×10 <sup>-2</sup>	[55]	DEA
-	PVDF	0	5wt% glycerol	2.00×10 <sup>-2</sup>	[53]	DEA
-	PVDF	0	5wt% LiCl	3.75×10 <sup>-2</sup>	[53]	DEA 🔂
-	PVDF	0	5wt% methanol	2.60×10 <sup>-2</sup>	[53]	DEA O
-	PVDF	0	5wt% phosphoric acid	2.70×10 <sup>-2</sup>	[53]	DEA
-	PVDF	0	-	2.70×10 <sup>-2</sup>	[53]	DEA
-	PEI	0	-	9.00×10 <sup>-3</sup>	[55]	DEA 🚺
-	PEI	0	5wt% PEG	2.35×10 <sup>-2</sup>	[55]	DEA 2
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**Table 4** Results of CO<sub>2</sub> stripping flux from DEA solution for different HFs

Mamhuana	Polymer	Air-gap			CO <sub>2</sub> flux	Defeneres	Liquid
Memorane	material	(cm)	Additive	(mol/m <sup>2</sup> .s)	Kelerence	absorbent	
$M_1$	PSf	0	1wt% SMM	5.30×10 <sup>-4</sup>	This work	Water	
$M_2$	PSf	5	1wt% SMM	4.70×10 <sup>-4</sup>	This work	Water	
M <sub>3</sub>	PSf	10	1wt% SMM	8.50×10 <sup>-4</sup>	This work	Water	
$M_4$	PSf	15	1wt% SMM	2.10×10 <sup>-3</sup>	This work	Water	
$M_5$	PSf	20	1wt% SMM	1.10×10 <sup>-3</sup>	This work	Water	
$M_6$	PSf	30	1wt% SMM	6.80×10 <sup>-4</sup>	This work	Water	
$M_7$	PSf	50	1wt% SMM	2.60×10 <sup>-4</sup>	This work	Water	
-	PSf	0	4wt% glycerol	1.30×10 <sup>-4</sup>	[54]	Water	
-	PVDF	0	5wt% glycerol	1.90×10 <sup>-3</sup>	[52]	Water	

**Table 5** Results of CO<sub>2</sub> stripping from water for different membranes

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Fig. 8 demonstrates the relationship between gas velocity and stripping flux for both DEA solution and water. The results for  $M_4$  membrane (15 cm air-gap) are plotted in the figure, but all other HFs would show a similar trend. As shown in Fig. 8, no noticeable stripping flux was perceived as the gas velocity was varied from 0.005 to 0.002 (m/s). This finding perfectly validates interpretations by Khaisri *et al.* that the liquid phase primarily governs mass transfer rate of MC stripping and the mass transfer resistance of gas stream has negligible effect on stripping flux.<sup>40</sup>



**Fig. 8** CO<sub>2</sub> stripping flux vs. gas velocity. ( $T_{DEA\& Water} = 80 \text{ °C}$ ,  $M_{DEA} = 1 \text{ mol/L}$ , liquid flow rate = 50 mL/min).

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The influence of liquid temperature on the stripping performance of M<sub>4</sub> membrane was 299 also studied and the results for water and DEA solution in Fig.9 and 10, respectively. As shown 300 in Fig. 9, a marked increase of stripping flux occurred from  $2.50 \times 10^{-4}$  to  $4.60 \times 10^{-2}$  (mol/m<sup>2</sup>.s) as 301 the temperature of water changed from 25°C to 80 °C, which can be attributed to the decrease of 302 CO<sub>2</sub> solubility as the water temperature increases.<sup>44,54</sup> Fig. 10 also shows that the stripping flux of 303 CO<sub>2</sub> increased as the DEA temperature was increased from 25°C to 80 °C. It could be said that 304 diffusion coefficient, equilibrium constant of chemical reaction and equilibrium partial pressure 305 of CO<sub>2</sub> are strongly influenced by liquid temperature.<sup>40</sup> A decrease in equilibrium constant of the 306 following reaction (equation 2) leads to enhancement of CO<sub>2</sub> partial pressure in the gas side by 307 the factor of 5 to 8 as the temperature is increased by 10 °C.<sup>56</sup> Consequently, an increase in 308 working temperature results in elevated driving force for CO<sub>2</sub> stripping from the DEA solution. 309 310

$$311 \quad \text{CO}_2 + 2R_2\text{NH} \leftrightarrow R_2\text{NH}_2^+ + R_2\text{NCOO}^-$$
(2)



Fig. 9 CO<sub>2</sub> stripping flux vs. liquid phase temperature (water) (liquid and gas flow rate = 200, 50 ml/min, respectively).





**Fig. 10** CO<sub>2</sub> stripping flux vs. liquid phase temperature (DEA) (liquid and gas flow rate = 200, 50 ml/min, respectively).

Fig.11 reveals the relationship between DEA concentration and stripping flux of  $M_4$  HF in the MC system. As illustrated in the figure an increase in DEA concentration from 0.25 to 1 M results in elevation of stripping flux, which can be validated by the reaction represented by equation 2. As it is interpreted by Rahbari-Sisakht *et al.*, increase of DEA concentration causes enhancement of absorbed CO<sub>2</sub> during preloading in the form of R<sub>2</sub>NCOO<sup>-</sup>ion.<sup>44</sup> During the stripping procedure, release of CO<sub>2</sub> causes the elevated CO<sub>2</sub> partial pressure at the interface, resulting in increase of driving force.<sup>40</sup>

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**Fig.11** CO<sub>2</sub> stripping flux vs. liquid velocity for various DEA concentration (gas flow rate =  $50 \text{ ml/min}, \text{T}=80 ^{\circ}\text{C}$ ).

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# 334 4. Conclusion

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TheSMM blended PSfHFs were spun with air-gaps of 0 to 50 cm and utilized to strip CO<sub>2</sub> by MC from DEA solution and water. M<sub>4</sub> membrane that was spun at 15 cm air-gap showed the highest stripping flux of  $4.60 \times 10^{-2}$  and  $2.10 \times 10^{-3}$  (mol/m<sup>2</sup>.s) for DEA solution and water, respectively, at

339	the	liquid velocity of 0.7 (m/s). Higher liquid velocities significantly increased stripping
340	flux	;however gas velocity exertedno significant influence, corroborating that liquid boundary
341	resi	stance is predominant. Additionally, it was foundthat the change in liquid temperature from
342	25°	Cto 80 °C increased the stripping flux from $2.50 \times 10^{-4}$ to $2.10 \times 10^{-3}$ mol/m <sup>2</sup> .s and $7.10 \times 10^{-3}$ to
343	4.60	$0 \times 10^{-2}$ mol/m <sup>2</sup> .s, for water and DEA solution, respectively. Increasing the DEA concentration
344	fror	n 0.25 to 1 mol/L, resulted in elevation of stripping flux from $1.70 \times 10^{-2}$ to $4.60 \times 10^{-2}$
345	(mo	d/m <sup>2</sup> .s) at DEA velocity of 0.7 m/s. Based on the experimental results, the data obtained
346	fror	nthe HF spun attheoptimum air-gap length (15 cm) surpassed the stripping flux data reported
347	in o	ther studies.
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