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4 **Facilitated transport membranes containing amino-functionalized multi-**
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6 **walled carbon nanotubes** for high-pressure CO₂ separations
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Abstract

In the present work, high-performance mixed matrix membranes containing amines have been developed for effective CO₂ removal at high pressures (15–28 bar) and high temperatures (103–121 °C). The membrane was synthesized by compatibly embedding amino-functionalized multi-walled carbon nanotubes (AF-MWNTs) as mechanical reinforcing fillers in the crosslinked polyvinylalcohol-polysiloxane/amine blend. The surface functionalization of MWNTs allows strong coupling with the hydrophilic membrane matrix to form a nano-reinforced facilitated transport membrane, which achieved exceptional CO₂ selectivity and permeability via the facilitated transport mechanism as well as attractive membrane stability via the incorporation of MWNTs. The synthesized membranes exhibited an average CO₂ permeability of 957 Barrers coupled with high selectivities vs. H₂ (56), CH₄ (264), and N₂ (384) at 107 °C and 15 bar. The effects of AF-MWNT loading, high molecular weight species content, selective layer thickness, feed pressure, relative humidity, and temperature on membrane performance were thoroughly studied for a fundamental understanding of membrane properties. Furthermore, a mathematical model has been used to describe and explain the thickness-dependent CO₂ transport behavior in the membrane. The combination of high CO₂ permeability and good selectivities vs. CH₄, H₂, and N₂, along with enhanced mechanical stability, makes the membrane a promising candidate for the gas separation applications at high pressures.

Keywords: Facilitated transport membrane; Amino-functionalized multi-walled carbon nanotube; CO₂ separation; High-pressure gas separation; Natural gas sweetening

1. Introduction

Natural gas is an important source for energy production nowadays. The natural gas purification industry offers a large market opportunity for gas separation technologies [1]. Although several contaminants are present in raw natural gas composition, carbon dioxide always constitutes the major impurity and its removal is of fundamental importance to meet the pipeline specification ($< 2\%$ of the total composition), increase the heating value of natural gas, minimize pipeline corrosion, and cut down energy costs for compression and delivery [2,3]. In addition, the removal of CO_2 is also an important separation step in other processes, e.g., the purification of shifted syngas to produce H_2 as fuel gas for gas turbines or fuel cells [4].

In addition to the available technologies such as potassium carbonate or amine absorption, pressure or temperature swing adsorption, and cryogenic distillation, polymeric membranes offer a potentially efficient strategy due to intrinsic advantages such as low energy consumption, small footprint, reduced waste production, and good processability [5]. The industrial viability of this technology relies strongly on robust materials that exhibit high permeability and selectivity along with necessary mechanical, thermal and chemical stabilities when exposed to typical operating conditions [6].

Facilitated transport (FT) membranes represent a unique group of polymer membranes. In FT membranes, the gas transport behavior is dominated by the facilitated transport mechanism, which exploits the fast chemical reactions between CO_2 and basic compounds (also called “carriers”) at the feed gas/membrane interface to enhance CO_2 trans-membrane flux [7].

The reaction between amines and CO_2 can be described by the zwitterion mechanism as shown in Eqs. (1) and (2). In the first step, a single amine molecule reacts with one CO_2

molecule to form a zwitterion intermediate, which is then deprotonated by a secondary amine to generate a carbamate ion.

For unhindered amines, the carbamate ion formed is rather stable, resulting in an overall reaction ratio of one mole of CO_2 to two moles of amines [8]. On the other hand, if the amine is sterically hindered, the bulky group on the amine moiety makes the carbamate ion unstable, which undergoes hydrolysis very quickly to give a bicarbonate ion and a free amine molecule as shown by Eq. (3):

As a result, the amine steric hindrance effect doubles the reaction sites available per unit volume of membrane matrix theoretically, hence enhancing the CO_2 transport rate across the membrane [9].

KOH can also act as a CO_2 carrier, reacting with CO_2 to produce potassium carbonate and potassium bicarbonate (K_2CO_3 and KHCO_3) based on a different reaction mechanism given by the following equation [10]:

After the reaction, the reaction products (i.e., carbamates, bicarbonates, K_2CO_3 , and KHCO_3) carrying CO_2 leave the feed gas/membrane interface and diffuse across the membrane selective layer along their concentration gradients. Only a small portion of CO_2 as well as the other non-reacting gaseous species (i.e., H_2 , CH_4 , and N_2) is transported across the membrane based on the solution-diffusion mechanism at a much lower flux.

Due to the fast, specific chemical reaction, facilitated transport membranes are able to couple high CO_2 trans-membrane flux and very good selectivity, going beyond the tradeoff limit between permeability and selectivity of solution-diffusion membranes [11–14].

Furthermore, the facilitated transport performance has demonstrated a close correlation with the type of amine carriers. Amine carriers can be classified into two groups. A mobile carrier is a small-molecule carrier with a bonded CO₂ reactive site, which is able to move freely across the selective layer. A fixed-site carrier is defined as a carrier having a long-chain polymer backbone with pendant CO₂ reactive sites that has limited mobility around its equilibrium position in the membrane. Zhao and Ho have reported that the facilitated transport membrane containing only fixed-site carriers (poly-N-isopropylallylamine) achieved a CO₂ permeability slightly higher than 300 Barrers (1 Barrer = $1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ or $3.364 \times 10^{-16} \text{ mol s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$) along with a CO₂/H₂ selectivity close to 45 and a CO₂/N₂ selectivity of 340 at 2 bar and 110 °C [9]. In another publication, the same group replaced part of the fixed-site carriers with mobile carriers and obtained a dramatically improved membrane performance (i.e., CO₂ permeability of 6500 Barrers and CO₂/H₂ selectivity of 340) under the same test conditions [15]. Similar results were also obtained by Zou et al. using facilitated transport membranes of a different composition with both mobile and fixed-site carriers [16]. These results highlight the significant contribution of mobile carriers to facilitated transport membrane performance.

Normally, facilitated transport membranes experience a performance drop (both CO₂ permeability and selectivity) with an increased feed pressure, due to the characteristic “carrier saturation” phenomenon of facilitated transport membranes [17]. For a given membrane, the total number of amine carriers available for the reaction with CO₂ is fixed. Under an increasing feed pressure or CO₂ partial pressure, more and more amine carriers are involved in the reactions, leading to an increasing CO₂ flux. When all the carriers are reacted, the CO₂ flux approaches to a nearly constant value with a minor increase due to the physical solution-diffusion transport. Further increasing feed pressure or CO₂ partial pressure thus results in a drop of CO₂ permeability [18]. Meanwhile, the solution-diffusion fluxes of other penetrants

(i.e., H₂, CH₄ and N₂) increase linearly with feed pressure, resulting in decreased CO₂ selectivities. Bai and Ho reported good results of crosslinked polyvinylalcohol-based (PVA-based) FT membranes, including a CO₂ permeability of about 300 Barrers and a CO₂/H₂ selectivity of 18 at 106 °C and a feed pressure of 29 bar [19]. Xing and Ho synthesized FT membranes containing fumed silica as reinforcing fillers and showed very promising results, including a CO₂ permeability of 1296 Barrers and a CO₂/H₂ selectivity of 87 at 107 °C and a feed pressure of 15 bar [20].

In spite of the outstanding separation performance, facilitated transport membranes still suffer from the instability issue, especially for high-pressure gas separations. Few publications have reported long-term stable performances of facilitated transport membranes for more than 400 h under low pressures (~2 bar) with different types of carriers [15,21]. At high pressure and high temperature conditions, the polymeric selective layer loses rigidity and becomes susceptible to compaction, causing a continuous decrease in the membrane separation performance over time [22,23]. Operated at 15 bar and 106 °C, the crosslinked PVA-based FT membrane without nanofillers underwent a continuous performance drop over 500 h, resulting in a total reduction of 13.1% in the CO₂ permeability and 19.6% in the CO₂/H₂ selectivity [23]. SEM images showed that the selective layer thickness was compressed by 50% after the 500-h test [23]. This instability issue clearly represents a serious threat to the viability of facilitated transport membranes for high-pressure gas separations.

The present work aims at demonstrating that facilitated transport membranes are able to exhibit desirable performances for high-pressure gas separation applications. For this reason, a new type of facilitated transport membrane with enhanced anti-compaction property and separation performance has been developed for high-pressure gas separations. Several strategies were used to manipulate the key membrane properties, especially mechanical

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4 strength, to obtain stable, efficient selective materials for CO₂ removal. Rigid multi-walled
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6 carbon nanotubes (MWNTs) were incorporated in the membrane matrix to enhance the
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8 overall membrane mechanical strength [24]. To maximally harness the outstanding
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10 mechanical and thermal properties, the naturally hydrophobic graphene wall of MWNTs was
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12 bonded with amine moieties to increase the affinity with the highly hydrophilic polymeric
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14 matrix and ensure a homogeneous dispersion in the membrane structure. Polyamines of high
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16 molecular weights were used as fixed-site carriers, whereas aminoacid potassium salt and
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18 potassium hydroxide were used as mobile carriers. The potassium hydroxide was used to
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20 catalyze the crosslinking of polyvinylalcohol and retained in the membrane. The reactive
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22 moieties available on both mobile and fixed carriers molecules made the main contribution to
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24 CO₂ facilitated transport. Crosslinked polyvinylalcohol-polysiloxane (PVA-POS) was used
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26 as matrix polymer to provide membrane structural integrity and thus membrane stability
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28 under high pressures up to 28 bar.
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34 Two gas mixtures simulating natural gas and shifted syngas compositions were used as
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36 feed gases for membrane gas permeation tests in order to evaluate the potential applications
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38 of this membrane material for natural gas sweetening and H₂ purification. For a fundamental
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40 understanding of material properties, the membrane performance was studied and optimized
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42 by tuning key fabrication and operation parameters. Finally, a mathematical model, proposed
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44 by Noble et al. [25], was used to describe the thickness-dependent gas transport behavior of
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46 the synthesized membranes.
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51 52 **2. Experimental**

53 54 *2.1. Materials*

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56 Polyvinylalcohol (Poval S-2217, 92% purity, MW 150,000, 87 – 89% hydrolyzed) was
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58 provided by Kuraray America Inc. (Houston, TX) as a copolymer of vinyl alcohol containing
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a minor amount of sulfonated groups [26]. Potassium hydroxide (KOH, pellets, $\geq 85\%$, MW 56.11), glutaraldehyde aqueous solution (50 wt%, MW 100.12), 2-aminoisobutyric acid (AIBA, 98%), 3-aminopropyltriethoxysilane (APTES, 99%), and ethylenediamine (EDA, $> 99.5\%$) were purchased from Sigma-Aldrich (Milwaukee, WI). Poly(allylamine hydrochloride) (PAA-HCl) with an average MW of 112,000 was purchased from Monomer-Polymer and Dajac Laboratories (Trevose, PA). Hydrochloric acid (36.5–38.0%, FW = 36.46), sulfuric acid (98%, FW = 98.08), nitric acid (2.6 M, FW = 63.01), and acetone (99.7%, FW = 58.08) were bought from Fisher Scientific Inc. (Pittsburgh, PA). Lupamin[®] 9095, given by BASF (Vandalia, IL, was a commercial product of an aqueous solution containing 7 wt% polyvinylamine (PVAm) and 14 wt% sodium formate [27,28]. The PVAm in Lupamin[®] 9095 was purified using ethanol precipitation [29]. AIBA and PAA-HCl were neutralized by KOH before usage by following the procedures reported in our previous work [9,15]. All the other chemicals were used without further processing.

The MWNTs (Graphistrength[®] C100) used in this work were donated by Arkema Inc. (Philadelphia, PA). They were 0.1–10 μm in length and 10–15 nm in diameter, and had >90 wt% purity.

A nanoporous polysulfone composite support (an average pore size of 10 nm and a thickness of 140 μm including non-woven fabric) was purchased from TriSep Corporation (Goleta, CA). A microporous polytetrafluoroethylene (PTFE) membrane (pore size ≥ 30 nm, thickness of 20 μm) was provided by W.L. Gore & Associates Inc. (Newark, DE).

Specialty gas cylinders containing certified-grade gas mixtures purchased from Praxair Inc. (Danbury, CT) were used as the feed gas. The dry gas compositions used in this work were: (1) 20% CO₂, 20.2% H₂, 59.8% CH₄ and (2) 20% CO₂, 40% H₂, 40% N₂. Pre-purified argon cylinders purchased from Praxair Inc. (Danbury, CT) were used as sweep gas.

2.2. Amino-functionalization of MWNTs

The raw MWNTs were functionalized by bonding amino groups on the graphene side walls and tube ends in order to increase their affinity with the hydrophilic membrane matrix.

The functionalization was carried out in two steps as shown in the scheme of Fig. 1.

In the first step, 500 mg raw MWNTs were added in a mixture of 90 ml H_2SO_4 and 30 ml HNO_3 [30,31] and the suspension was refluxed in a round-bottom flask at 120 °C for 90 min. After the reaction, the suspension was cooled to room temperature. The residual acids were removed and the products were washed with reverse osmosis (RO) water in a vacuum filtration using the microporous PTFE membrane until the filtrate pH reached a constant value. The resulting acid-treated MWNTs (AT-MWNTs) were dispersed in RO water using a ultrasonication bath (FS-30, 130 W, Fisher Scientific) until an aggregation-free dispersion (1 wt% AT-MWNTs) was achieved. The AT-MWNTs concentration was determined by the drying method, i.e., weighing a certain amount of AT-MWNTs solution (about 1 g), removing all the water at 105 °C for 3 h, and weighing the dry mass.

In the second step, the surface $-\text{COOH}$ and $-\text{OH}$ moieties on the prepared AT-MWNTs were further modified via condensation of small aminosilane molecules to obtain the amino-functionalized MWNTs (AF-MWNTs) [32,33]. APTES was dissolved in acetone under stirring to prepare a 5 wt% solution. The APTES-acetone solution was then mixed with the prepared AT-MWNT dispersion at a weight ratio of 1:10 (APTES/AT-MWNT) and heated at 80 °C for 30 min under vigorous stirring. Acetone was selected as the solvent for APTES instead of water to prevent fast polycondensation of $-\text{OH}$ groups in aqueous solution [34]. Finally, the reaction solution was ultrasonicated for 60 min, followed by centrifugation at 8000 rpm for 2 min to remove aggregates and particles. The AF-MWNT concentration in the centrifuged dispersion was measured by the drying method aforementioned, normally within the range of 0.6–1 wt%.

2.3. Membrane synthesis

In the present work, mixed matrix membranes were prepared by the solution casting technique. The casting solution, prepared by homogeneously dispersing AF-MWNTs in crosslinked PVA-POS/amine aqueous solution, was cast on a nanoporous polysulfone support. After water evaporated, a thin mixed-matrix selective layer was formed on the support.

The crosslinked PVA-POS was synthesized by a two-step approach. In the first step, 3.3 g of PVA were completely dissolved in 18 g of water under stirring at room temperature overnight. One gram of APTES as well as a small amount (0.13 g) of HCl was added to the aqueous PVA solution. The mixture was vigorously stirred at 80 °C for 80 min. An acid-catalyzed sol-gel reaction took place, generating a PVA-POS network through the polycondensation between hydroxyl groups on PVA and APTES [20]. PVA has been demonstrated to be very stable in both acid and alkaline environments [35].

The second step involved a KOH-catalyzed crosslinking reaction, using glutaraldehyde as the crosslinking agent. Firstly, 2 g of KOH aqueous solution were added to the aqueous PVA-POS solution and stirred at 80 °C for 15 min to neutralize HCl. Afterwards, a stoichiometric amount of glutaraldehyde, for a 100 mol% crosslinking degree for PVA, was added to the solution under stirring. The crosslinking reaction was carried out at 80 °C for 2.5 h under vigorous stirring. The reaction scheme has been described in previous publications [15,20]. The preparations of aqueous solutions of 2-aminoisobutyric acid potassium salt (AIBA-K) and polyamine can also be found in prior work [9,15,20].

In order to prepare the casting solution, a calculated amount of the prepared AF-MWNT dispersion was added to the crosslinked PVA-POS solution under stirring to obtain a well-mixed solution. The mixture was then ultrasonicated to ensure a good dispersion of AF-

MWNTs. Based on the desired membrane composition, calculated amounts of EDA, polyamine solution, AIBA-K solution, KOH solution were sequentially added to the solution. Vigorous stirring was maintained during the operation to obtain a homogenous solution without gelling. AIBA-K (a sterically hindered amine) and KOH acted as mobile CO₂ carriers in the membrane, whereas one of the three unhindered polyamines (i.e., PAA, Lupamin[®] 9095, and purified PVAm from Lupamin[®] 9095) was used as the fixed-site carrier.

The homogeneous casting solution was cast on a flat-sheet polysulfone support by means of a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The cast membrane was immediately dried by convective air flow at 105 °C for 20 min for a fast water removal, followed by thermal curing in a muffle oven at 120 °C for 6 h to completely remove the solvent and complete the crosslinking reaction of PVA with glutaraldehyde. EDA was completely removed from the membrane during the curing process due to its boiling point (108 °C) [36]. The solid membrane compositions used in the present work are listed in Table 1.

2.4. Membrane characterization

The surface chemical groups on raw MWNTs, AT-MWNTs, and AF-MWNTs were characterized by Fourier transform infrared (FTIR) spectroscopy using a Nicolet 470 FTIR spectrometer (Thermo Electron Co., Waltham, MA) to confirm the successful functionalization. To prepare FTIR samples, each type of nanotubes was ground, mixed with KBr at a weight ratio of 1:20 (MWNT to KBr), and pressed into pellets.

The total thickness of each solid membrane was measured by a Mitutoyo electronic indicator (Model 543-252B, Mitutoyo America Corp, Aurora, IL) with an accuracy of ±0.5 µm. The thickness of the selective layer was calculated by subtracting the polysulfone support thickness from the total thickness.

The membrane sample with a test area of 5.7 cm² was held in a circular stainless steel cell and tested under a countercurrent flow pattern between the feed and the sweep gas streams in order to maximize the driving force across the membrane. Both the feed-side and the sweep-side relative humidities (RHs) were controlled by highly precise piston metering pumps (Varian ProStar, Model 210, Varian Inc., Palo Alto, CA). The retentate- and permeate-side gas samples were analyzed online by a gas chromatograph (Agilent 6890N, Agilent Tech., Palo Alto, CA). A scheme of the gas permeation apparatus as well as detailed operation procedures can be found in previous publications [9,15,20]. The membrane separation performances in this work were characterized by CO₂ separation factor α vs. CH₄ (or H₂, N₂) and CO₂ permeability P defined as follows:

$$\alpha_{i,j} = \frac{y_i/y_j}{x_i/x_j} \quad (5)$$

$$P_i = \frac{N_i \cdot \ell}{\Delta p_i} \quad (6)$$

where i denotes the gas component CO₂ and j denotes another gas component (CH₄, H₂, or N₂), y and x are the mole fractions of each gas component in the sweep and feed sides of the membrane, respectively, N_i is the steady-state CO₂ molar flux across the selective layer, and ℓ is the selective layer thickness. The pressure difference across the membrane, Δp_i , represents the driving force for the permeation process, which is determined using the logarithmic mean method in the present work as shown in Eq. (7):

$$\Delta p_i = \frac{(p_{i,\text{feed in}} - p_{i,\text{sweep out}}) - (p_{i,\text{feed out}} - p_{i,\text{sweep in}})}{\ln(p_{i,\text{feed in}} - p_{i,\text{sweep out}}) - \ln(p_{i,\text{feed out}} - p_{i,\text{sweep in}})} \quad (7)$$

The common unit of P is Barrer, which corresponds to 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ or 3.364 × 10⁻¹⁶ mol · s⁻¹ · m⁻¹ · Pa⁻¹. (P/ℓ) is referred as the permeance, and its common unit is GPU (gas permeation unit), which is 10⁻⁶ cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹. In this

work, selectivity (or “permselectivity”), which is the ratio of permeabilities, is considered to be equal to separation factor and calculated by Eq. (5) because the partial pressure of the considered gas on the permeate side was negligible with respect to its partial pressure on the feed side [5].

3. Results and discussion

3.1. FTIR characterization of MWNT surface functionalization

Fig. 2 depicts the FTIR spectra of raw MWNTs and the two functionalized MWNTs, i.e., AT-MWNTs and AF-MWNTs. The spectrum of raw MWNTs is presented in Fig. 2a, which identifies two groups of peaks: (1) the C=C bond peaks at 1632 cm^{-1} and 1500 cm^{-1} and (2) the C–H alkyl bond peaks in the region of $2923\text{--}2850\text{ cm}^{-1}$ [37]. The first group of peaks shows the typical carbon skeleton (graphene) in the MWNT structure, whereas the second group corresponds to the presence of defects in the nanotube walls and tube ends generated from the fabrication process.

The strong acid oxidation introduced carboxylic acid groups and hydroxyl groups on MWNTs surface. As shown in the FTIR spectrum of AT-MWNTs (Fig. 2b), three new peaks appear at 1708 cm^{-1} related to the C=O stretching vibration of –COOH, 1384 cm^{-1} in correspondence to the O–H bending deformation of –COOH and/or –OH, and 1166 cm^{-1} for the C–O stretching in –COOH [30,33,38]. The presence of these new chemical groups confirms the effective surface functionalization of the nanotubes.

Fig. 2c shows the spectrum of the AF-MWNTs. Compared with Fig. 2b, the peak at 1166 cm^{-1} , which represents the C–O stretching in –COOH, decreases and two new shoulders appear at 1047 cm^{-1} and 1102 cm^{-1} , corresponding to the new Si–O–C and Si–O–Si bonds, respectively [20]. The presence of these new bonds confirms the occurrence of the

condensation reaction between –OH/–COOH of AT-MWNTs and silanol [32,33]. Thereby, the amino groups from APTES were successfully grafted on MWNT surface.

3.2. Membrane performance at different feed pressures and membrane composition optimization for high-pressure operation

Facilitated transport membranes are known to be able to couple very high CO₂ selectivity vs. non-reacting species with high CO₂ permeability, due to the aforementioned chemical reactions between CO₂ and carriers (amines and KOH) present in the membrane matrix. At low-pressure operations (~2 bar), remarkable performances have been reported for CO₂/H₂ [15,16] and CO₂/N₂ [39,40] separations.

In this work, the membrane sample M-01 (see Table 1) containing 2.1 wt% AF-MWNTs was first synthesized and tested at 107 °C and a low feed pressure of 2 bar. The test results as well as operating conditions are shown in Table 2. The dry membrane contained 22.3 wt% Lupamin[®] 9095 (the commercial composition of the product contains a mixture of PVAm and sodium acetate [27]) as the fixed-site carrier. In the literature, different polyamines, such as PAA, sterically hindered polyamines, polyethylenimine (PEI), have been used as fixed-site carriers for facilitated transport membranes [9,15,16,41]. Nevertheless, the use of polyvinylamine is rare [21,42]. Polyvinylamine is an unhindered primary amine with one pendant amino group attaching to each repeating unit (CH–CH₂). Theoretically, the denser amino groups in PVAm over PAA and PEI increase the reactive sites available for the reaction with CO₂ and are therefore able to enhance the membrane performance. According to the results obtained in this work, the membrane M-01 containing Lupamin[®] 9095 demonstrated a CO₂ permeability (3157 Barrers) similar to that of the membrane containing PAA [15], but a higher CO₂/H₂ selectivity (198) at 2 bar and 107 °C. Zou et al. have reported

an even higher CO₂/H₂ selectivity using a thicker membrane containing PAA tested at similar operating conditions [16].

In order to deal with the compaction and instability issues for high-pressure gas separations, the solid membrane composition was optimized by adjusting the high molecular weight species (HM_WS) content to improve the membrane structural integrity. As shown in Table 1, the typical solid membrane composition developed by the present work consists of a crosslinked PVA-POS network as the supporting matrix, AF-MWNTs as mechanical reinforcing fillers, AIBA-K and KOH as the mobile carriers, and polyamine as the fixed-site CO₂ carrier. We define the HM_WS content as the total solid concentration of crosslinked PVA-POS and polyamine. The two polymers combined via entanglement and hydrogen bonding to construct the fundamental matrix that retained other components and supported the whole membrane structure. Three polyamines were used in this work: Lupamin[®] 9095 (commercial PVAm solution with dry composition of 33.3 wt% PVAm and 66.7 wt% sodium acetate [27]), purified Lupamin[®] 9095 (by the ethanol precipitation method [29], resulting in a dry composition of 66.7 wt% PVAm and 33.3 wt% sodium acetate), and PAA (98% purity).

The resulting membranes with various HM_WS contents (see M-02 to M-11 in Table 1) were tested at 15 bar and 107 °C. The test results can be found in Table 2. Fig. 3 depicts the membrane CO₂/H₂ selectivity as a function of HM_WS content and clearly shows the key role of HM_WS content as well as structural integrity to the membrane gas transport properties. The specimens containing less high M_W species (M-02 to M-05) exhibited much lower CO₂/H₂ selectivities than our previous results [20]. Moreover, during the gas permeation tests, their CO₂ permeabilities were observed to decrease after few hours at steady state. In addition, when the specimen was removed from the sample holder after each test, brownish spots of oxidized amines were found on the back of the membrane, giving evidence of carrier leakage from the weak membrane structure despite the 100% crosslinking degree of the

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4 PVA-POS network. According to Table 1, the membranes M-02 and M-03 contained
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6 Lupamin[®] 9095 as fixed-site carriers, resulting in an HM_WS content of <35 wt% due to the
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8 large amount of sodium formate. The low HM_WS content was likely responsible for the poor
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10 membrane performance. The samples M-04 and M-05 containing purified Lupamin[®] 9095
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12 had limited increases in HM_WS contents (~40 wt%) and therefore still obtained poor
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14 separation performances.
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18 Large HM_WS contents (51–56.5 wt%) were achieved in the specimens M-06 to M-11
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20 using PAA at 98% purity as fixed-site carriers. The large HM_WS content, together with the
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22 compatible incorporation of AF-MWNTs, contributed to a significant improvement in the
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24 membrane performance at high pressure and high temperature. An average CO₂ permeability
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26 of 957 Barrers with high selectivities (56 vs. H₂, 264 vs. CH₄, 384 vs. N₂) were achieved at
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28 15 bar and 107 °C. More importantly, the membrane stability was dramatically improved,
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30 reaching a stable gas separation for over 18 h. A high content of long-chain polymers in the
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32 membrane composition enhanced the rigidity and structural integrity of polymeric matrix for
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34 high-pressure, high-temperature tests. Water-induced swelling and carrier leakage were
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36 thereby inhibited.
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41 These membranes also demonstrated CO₂/CH₄ separation performance well beyond the
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43 permeability-selectivity tradeoff, represented by the Robeson's upper bound [12] shown in
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45 Fig. 4. These results stand for a significant contribution to the state of the art of gas
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47 separation membranes. In addition, since the amine-CO₂ reaction in the membrane is
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49 facilitated by water, no dehydration step is required before the membrane module, which
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51 simplifies the separation process, making these membranes an attractive technology for
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3.3. Membrane performance at 28 bar

Further increasing the HM_WS content to >70 wt% by doubling the PAA content generated robust facilitated transport membranes (i.e., M-14 to M-16 in Table 1) that could withstand a pressure as high as 28 atm and a temperature of 107 °C. The membrane M-14 containing 46.4 wt% PAA, 10.6 wt% KOH, and 10.8 wt% AIBA-K exhibited a stable CO₂ permeability of 224 Barrers along with a CO₂/H₂ selectivity of 16 and a CO₂/N₂ selectivity of 139 for over 24 h.

At the same HM_WS amount, replacing the amine mobile carrier AIBA-K with KOH in the composition of M-15 resulted in a higher CO₂ permeability (i.e., 326 Barrers) without any detriment to membrane selectivities (i.e., 15 vs. H₂, 147 vs. N₂), suggesting the higher facilitated transport efficiency of KOH. For M-16, an additional increment of KOH content at the expense of PAA content led to a further improvement of CO₂ permeability to 440 Barrers. Meanwhile, the reduced HM_WS amount (i.e., 70.8 wt%) might impact the membrane structural integrity, causing slightly decreased CO₂ selectivities (i.e., 13 vs. H₂, 128 vs. N₂) of M-16.

The facilitated transport membrane performance with feed pressure varying in the range of 2–28 bar is shown in Fig. 5. As can be seen, the CO₂ permeability and selectivities vs. H₂ and N₂ decreased with an increasing feed pressure due to the “carrier saturation” described in the introduction section.

3.4. Effect of AF-MWNT loading at 15 bar

Continued efforts have been made in incorporating carbon nanotubes (CNTs) in polymer membranes for gas permeation and mechanical reinforcement purposes. Previous results found that the poor compatibility of carbon nanotubes with polar polymers led to the formation of nanogaps and voids between the CNT surface and polymer chains as more

CNTs were incorporated, which adversely affected membrane selectivity. Kim et al. reported a significant increase (up to 70%) of the storage modulus after the addition of 5–15 wt% of octadecyl ammonium-modified single-wall nanotubes (SWNTs) [43,44]. In addition, they showed an increase in the permeability of all the investigated gaseous probes, which was more evident for the less permeable species. Hence, the separation factor was usually reduced with increasing the loading content in the membrane composition. The same effect was also observed by Choi et al. in pervaporation membranes containing acid-treated MWNTs [45]. When increasing the acid-treated MWNT amount, they found a significant increase in the solute flux across the selective layer with a simultaneous decrease of water/ethanol selectivity. Ge et al. analyzed the gas transport properties of pure poly(ether-sulfone) (PES) membrane and PES membrane containing functionalized MWNTs and concluded that the increased gas diffusion in MMMs came from the gas transport through the voids/nanogaps between the incompatible MWNT surface and polymer chains [46]. As claimed by Cong et al., the size of nanogaps played a key role for the separation performances of mixed matrix membranes [38]. In the previous publications by our group raw MWNTs were incorporated in facilitated transport membranes made of highly hydrophilic polymers [22,47]. The membranes showed a decreased selectivity as the loading of hydrophobic nanofillers was increased.

In this work, the surface chemistry of MWNTs was modified to allow strong binding with the polymer network. The surface amino groups of AF-MWNTs allow strong coupling with the hydrophilic polymer chains abundant of hydroxyl- and amino-pendent groups and thereby suppressed the formation of nanogaps effectively. In addition, these surface amino groups might also be involved in the crosslinking reaction during the 120 °C thermal curing process, forming chemical bonds with the polymer network.

The strong coupling dramatically enhanced the affinity of naturally hydrophobic MWNTs with the highly hydrophilic membrane matrix, enabling a compatible incorporation. The CO₂/H₂ selectivity, CO₂/CH₄ selectivity, and CO₂ permeability at 15 bar and 107 °C are presented as a function of amino-functionalized MWNT (AF-MWNT) loading in Fig. 6. As the AF-MWNT loading was increased up to 6.9 wt%, the CO₂/H₂ and CO₂/CH₄ selectivities as well as the CO₂ permeability showed limited variations. The CO₂/H₂ selectivity remained unchanged at 54, whereas the CO₂/CH₄ selectivity was slightly decreased by 6.5%. The CO₂ permeability was increased by < 4%. Thus, the nanocomposite membranes containing AF-MWNTs can be made mechanically robust without adversely affecting their CO₂ separation performance.

3.5. Effect of sweep-side RH on membrane performance at 15 bar

The presence of water is crucial for the facilitated transport membranes, because water participates in the reversible CO₂-amine reaction (i.e., the hydrolysis of zwitterion and carbamate ions). As a result, the highly hydrophilic membrane matrix was swollen during the gas permeation test [21], resulting in a different mobility of reaction products as well as gas molecules from that in a dry membrane.

From this point of view, the correlation of membrane performance with water retention in the membrane matrix was studied by varying the relative humidity (RH) on the sweep side. The feed and sweep gas streams in the permeation apparatus were moisturized in their respective humidifiers before contacting the membrane. The water retention in the membrane matrix was thereby governed by relative humidities of the gas streams. We studied the membrane separation performance at 107 °C and 15 bar with the RH varying from 47% to 80% (i.e., 47%, 60%, 72% and 80%) in the sweep gas by adjusting the liquid

water delivery rates (i.e., 0.03, 0.06, 0.15 and 0.52 cm³/min). The feed stream was kept saturated.

As illustrated in Fig. 7, the membrane performance including CO₂ permeability and CO₂/CH₄ and CO₂/H₂ selectivities increased **monotonically** with the sweep RH in the range of 47–72% and reached 980 Barrers, 266, 53, respectively, at 72% RH. As the sweep RH was further increased to 80%, the CO₂ permeability went higher to 1147 Barrers, almost 5 times that obtained at 47% RH (234 Barrer). The above results demonstrated the dramatic enhancement of RH on CO₂ facilitated transport. An increased RH led to a higher water content in the membrane matrix, which accelerated the reaction between CO₂ and amine carriers and enhanced the mobilities of reaction products and unreacted CO₂ [15,17]. This is an attractive property to industrial gas separation such as natural gas sweetening, because no dehydration step is required before the membrane module, which simplifies the process and reduces energy and cost.

Fig. 7 also shows that the CO₂/CH₄ and CO₂/H₂ selectivities increased along with the CO₂ permeability up to a 72% RH, reaching a maximum, and then dropped to 227 and 49, respectively, at a high RH of 84%. At such a high RH, a severe water-induced swelling of the hydrophilic matrix occurred [21], which impaired the barrier property of the crosslinked PVA-POS network and thereby triggered the considerable increases in H₂ and CH₄ permeabilities. The same trend in CO₂/H₂ selectivity was also observed by Xing and Ho using facilitated transport membranes containing fumed silica tested at 15 bar [20]. For low-pressure (2 bar) tests, our previous results showed a **monotonic** increase of membrane selectivity as well as permeability with RH [15–17]. Therefore, we believe that this unfavorable selectivity drop at a high RH was associated with feed pressure and a high feed pressure enhanced the penetration of non-reacting gas molecules.

3.6. Effect of temperature on membrane performance at 15 bar

Membranes for industrial gas purification are expected to be operated at high temperatures above 100 °C in order to prevent condensation of impurities within the membrane unit and to facilitate the separation process [48–50]. However, few data on membrane performance at such severe conditions can be found in the literature. In order to evaluate the potential of our membranes for industrial applications, we also studied the membrane performance, including CO₂ permeability and CO₂/H₂ selectivity, at 15 bar and temperatures of 103–121 °C using two membranes M-10 and M-11. All the other operating conditions are shown in Table 3.

The gas permeation results are presented in Fig. 8 as well as Table 3. As shown in Fig. 8, both the CO₂/H₂ selectivity and CO₂ permeability first increased with temperature at 103–107 °C and reached their maximum values (54 and 886 Barrers, respectively) at 107 °C, followed by continuous decreases at 107–121 °C. From 107 to 121 °C, the membrane permeability was reduced by 50% while the selectivity experienced a slighter reduction by 11%. In line with the water-induced membrane swelling, the H₂ permeability demonstrated a **monotonic** decrease (~50%) over the entire range of 103–121 °C (data not shown).

The different permeability profiles can be explained by the temperature effects on different gas transport mechanisms. Temperature affects the facilitated transport in two competing ways: on one side, temperature accelerates the CO₂-amine reaction kinetics as well as the diffusion of reaction products across the membrane; on the other side, it causes a decrement of water retention in the membrane (owing to the lower relative humidity shown in Table 3), which in turn hinders the reaction and diffusion. As discussed in Section 3.5, a decreased RH significantly hindered the CO₂ facilitated transport across the selective layer and hence the overall membrane performance. For CO₂ transport, the stimulating effects of temperature on reaction and diffusion prevailed in 103–107 °C, while water retention in the

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4 membrane matrix, governed by the temperature-dependent RH, controlled CO₂ permeability
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6 in 107–121 °C. For the physical solution-diffusion of H₂, the high temperature significantly
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8 reduces its solubility and also impairs its diffusion across the less swollen membrane,
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10 resulting in a **monotonic** decrease in 103–121 °C.
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13 This investigation determined that 107 °C was the optimal operating temperature for the
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15 particular membrane composition developed by this work. The robust nanocomposite
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17 structure enabled the facilitated transport membranes to survive at a pressure as high as 15
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19 bar and temperature as high as 121 °C and demonstrate good selectivities of 48 vs. H₂ and
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21 251 vs. CH₄.
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24 Such an optimal operating temperature has been reported in the literature of other
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26 facilitated transport membranes. For example, the optimal temperature was 100 °C for the
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28 sulfonated polybenzimidazole copolymer-based membrane [51], 107 °C for the crosslinked
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30 PVA-POS/fumed silica MMMs [20], and 110 °C for the membranes based on chitosan [52].
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32 For the same membrane composition, the optimal temperature varied with feed pressure. For
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34 example, the optimal temperature was 110 °C for the crosslinked PVA/amine membrane
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36 tested at a feed pressure of 2 bar [17], but changed to 106 °C when operated at 15 bar [19].
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38 These results suggest that the optimal operating temperature for a certain membrane has a
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40 close correlation with its water retention capacity, determined by the membrane
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42 composition/hydrophilicity, as well as the operating conditions. It is necessary to determine
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44 this temperature for scaled-up facilitated transport membranes to obtain the best separation
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54 *3.7. Effect of membrane thickness on separation performance at 15 bar*

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56 A series of membranes with different selective layer thicknesses (9–29 μm) were
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58 synthesized using the same composition (see M-08 in Table 1) and tested at the same
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conditions (15 bar and 107 °C) to investigate the effect of selective layer thickness on the membrane performance. Key gas permeation properties of CO₂ permeability and permeance and CO₂ selectivities vs. H₂ and CH₄ are presented in Figs. 9 and 10, respectively, as a function of selective layer thickness.

Fig. 9 depicts the variation of CO₂ permeability and permeance in the investigated range (9–29 µm). As expected, increasing the selective layer thickness decreased the permeance from 45 GPU to 33 GPU. However, surprisingly, the CO₂ permeability was increased from 415 Barrers to 962 Barrers. Also affected were the selectivities as shown in Fig. 10. Since the permeabilities of solution-diffusion species (i.e., 2.9 Barrers for CH₄ and 15.3 Barrers for H₂) remained constant over the inspected thickness range, the increased CO₂ permeability resulted in overall increments of the selectivities along with the selective layer thickness.

The thickness-dependent CO₂ permeability is rarely reported in the literature [41,53]. This phenomenon could be explained by the complex gas transport mechanism in a facilitated transport membrane, which involves both the reversible reaction and the solution-diffusion. The bulk CO₂ transport starts with the sorption of CO₂ molecules and reactions with amine carriers at the feed gas/membrane interface, followed by the diffusions of reaction products along their respective concentration gradients across the membrane to the permeate side, where the CO₂ molecules are released into the sweep gas via the reversible reactions. Meanwhile, a small portion of CO₂ permeates by following the solution-diffusion mechanism [5].

The thickness-dependent CO₂ permeability can be explained by the mathematical model developed by Noble et al. [25]. The solid and dash lines in Figs. 9 and 10 represent the modeling correlations. This mathematical model can be used to describe the facilitated transport for negligible external mass-transfer resistances on both sides of the membrane.

The facilitation factor F , defined as the ratio of the total solute flux (N_{TOT}) to the solution-diffusion flux (N_{SD}), can be expressed by the following equation:

$$F = \frac{N_{\text{TOT}}}{N_{\text{SD}}} = \frac{1 + \frac{\alpha K}{1 + K}}{1 + \frac{\alpha K}{1 + K} \frac{\tanh(\lambda)}{\lambda}} \quad (8)$$

In Eq. (8), α is the mobility ratio (related to $D_{\text{AB}}/D_{\text{A}}$ where D_{AB} is the diffusion coefficient of the CO_2 -carrier reaction products and D_{A} is the diffusion coefficient of CO_2), K is the dimensionless equilibrium constant, and λ is defined as:

$$\lambda = \frac{1}{2} \cdot \left(\frac{1 + (\alpha + 1)K}{\varepsilon(1 + K)} \right)^{0.5} \quad (9)$$

The thickness dependence of F is expressed by ε , the inverse of the Damköhler number. ε is the ratio of diffusive mass transport rate to reaction rate:

$$\varepsilon = \frac{D_{\text{AB}}}{k_{\text{r}} \cdot \delta^2} \quad (10)$$

where k_{r} is the constant for the reverse reaction and δ is the selective layer thickness. In this way, the facilitation factor F , which represents the contribution of CO_2 -amine reaction to the overall transport, is thus thickness dependent.

With the assumption that a single overall reaction is sufficient to describe the CO_2 transport in the studied membranes, the model could be used to describe the experimental data obtained as shown by the solid and dash lines from the model in Figs. 9 and 10. The solid line in Fig. 9 was obtained using Eq. (8) for the F evaluation, which correlates with permeability via the following equation:

$$P_{\text{CO}_2} = \frac{N_{\text{TOT}} \cdot \delta}{\Delta p_{\text{CO}_2}} = \frac{N_{\text{SD}} \cdot F \cdot \delta}{\Delta p_{\text{CO}_2}} = P_{\text{CO}_2}^{\text{SD}} \cdot F \quad (11)$$

where $P_{\text{CO}_2}^{\text{SD}}$ is the CO_2 solution-diffusion permeability. The CO_2 permeance was finally obtained by dividing the permeability by the thickness of the selective layer as shown in the

dashed line in this figure. The solid and dash lines from the model in Fig. 10 were obtained by dividing the CO₂ permeability from Fig. 9 by the CH₄ permeability (2.9 Barrers) and by the H₂ permeability (15.3 Barrers), respectively. For the test conditions used in this work (i.e., partial pressures of species i and j on the downstream side were negligible compared to their counterparts on the upstream side), the permeability ratio provided a good representation of the real separation factor calculated by Eq. (5).

The CO₂ transport is assumed to take place mainly in the water-filled domain of the high hydrophilic membrane matrix. Therefore, α and K are fixed at 15 and 5, respectively, as suggested by Kemena et al. [54], while D_{AB} is set to be $3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at the same order of magnitude of the ion diffusivity in water [55]. The reverse reaction constant k_r suitable for the CO₂-amine reaction is 110 s^{-1} [56,57]. Finally, the solution-diffusion CO₂ permeability $P_{CO_2}^{SD}$ through the crosslinked PVA-POS based facilitated transport membrane is set at 150 Barrers, which is reasonable considering the CO₂ permeability in pure PVA membranes under saturation conditions [58] or in pure water [59]. The complete set of parameters used in the simulation is listed in Table 4.

The good agreement between the experimental and modeling results suggests that the thickness-dependent CO₂ permeability might be an intrinsic feature of the facilitated transport mechanism, in which the CO₂ transport mainly depends on the CO₂-carrier reaction rate and on the diffusivity of the reaction product. The physical solution-diffusion mechanism only contributes to a very small portion of the total CO₂ transmembrane flux. It is noted that Damköhler numbers calculated from the parameters in Table 4 and experimental data were always higher than 1, indicating that the reaction rate was higher than the diffusion rate of the reaction complexes and the latter was the rate-control step of the overall CO₂ transport across the membrane.

4. Conclusions

This work developed advanced facilitated transport membranes made of robust polymer-MWNT nanocomposite matrix containing amines for gas separations at high pressures (15–28 bar) and high temperatures (103–121 °C). The compatible incorporation of amino-functionalized MWNTs in the membrane matrix made of high molecular weight polymers significantly improved the membrane rigidity and structural integrity for a stable CO₂ removal at high pressures. The synthesized membranes demonstrated an average CO₂ permeability of 957 Barrers coupled with high selectivities vs. H₂ (56), CH₄ (264), and N₂ (384) at 107 °C and 15 bar, and achieved a CO₂ permeability of 224 Barrers along with CO₂/H₂ selectivity of 16 and CO₂/N₂ selectivity of 139 at 107 °C and 28 bar. The membrane performance was further studied and optimized by tuning key fabrication and operation parameters including AF-MWNT loading, HM_wS content, selective layer thickness, feed pressure, relative humidity, and temperature. A mathematical model was used to describe and explain the thickness-dependent CO₂ transport behavior.

The combination of high CO₂ permeability and good selectivities vs. CH₄, H₂, and N₂, along with enhanced mechanical property, makes these membranes promising candidates for the gas separation applications at high pressures.

Acknowledgement

The authors would like to thank W.L. Gore & Associates Inc. in Newark, DE for providing the microporous PTFE membrane, Arkema Inc. in Philadelphia, PA for giving MWNTs and Kuraray America Inc. in Houston, TX for donating PVA. The authors would like to gratefully acknowledge the Marco Polo Program of the University of Bologna for the travel funding support of the first author. The authors would also like to gratefully acknowledge the Department of Energy/National Energy Technology Laboratory (DE-FE0007632), the Office

of Naval Research/DJW Technology (N00014-14-C-098), the National Science Foundation (CBET 1033131 and IIP 1127812), and the Ohio Development Services Agency (OOE-CDO-D-13-05) for their financial support of this work. This work was partly supported by the Department of Energy under Award Number DE-FE0007632 with substantial involvement of the National Energy Technology Laboratory, Pittsburgh, PA, USA.

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Table 1. Solid compositions of MMMs synthesized in this work containing different types of polyamines (PAm): A = Lupamin[®] 9095, B = purified Lupamin[®] 9095, and C = PAA.

Sample No.	PAm Type	PVA (wt%)	AF-MWNTs (wt%)	KOH (wt%)	APTES (wt%)	PAm (wt%)	AIBA-K (wt%)	HM _W S (wt%)
<i>Membrane performance at 2 bar</i>								
M-01	A	20.2	2.1	19.0	5.4	22.3	31.0	32.9
<i>Membrane performance at 15 bar – Effect of HM_WS</i>								
M-02	A	20.5	2.2	16.8	5.2	23.6	31.7	33.5
M-03	A	22.8	1.9	19.3	0.2	28.2	27.6	32.3
M-04	B	20.9	2.2	17.6	5.3	24.4	29.7	37.0
M-05	B	23.6	2.4	14.8	4.9	29.3	25.0	42.9
M-06	C	25.2	2.5	19.4	5.2	20.9	26.8	51.3
M-07	C	24.1	2.4	17.7	5.0	24.0	26.7	53.2
M-08	C	23.3	2.3	17.1	6.1	25.8	25.4	55.2
M-09	C	24.0	2.4	16.3	6.1	26.4	24.8	56.5
M-10	C	23.7	2.4	16.5	6.0	26.1	25.4	55.8
M-11	C	23.6	2.3	16.7	6.3	26.2	25.0	56.0
<i>Membrane performance at 15 bar – Effect of MWNTs loading</i>								
M-12	C	24.2	0.0	17.1	6.4	25.5	26.8	56.1
M-13	C	22.9	6.9	15.6	5.8	25.2	23.6	53.9
<i>Membrane performance at 28 bar</i>								
M-14	C	23.6	2.3	10.6	6.3	46.4	10.8	76.2
M-15	C	23.6	2.3	21.4	6.3	46.4	0.0	76.2
M-16	C	23.6	2.3	26.8	6.3	41.0	0.0	70.8

Table 2. Gas transport results of membranes tested under different feed pressures (the membrane compositions are shown in Table 1).

Sample	ℓ	Feed p	CO ₂ Perm	CO ₂ /H ₂	CO ₂ /N ₂	CO ₂ /CH ₄
No.	(μm)	(bar)	(Barrer)	-	-	-
<i>Membrane performance at 2 bar</i>						
M-01 ^{a,b}	16	2	3157	198	380	650
<i>Membrane performance at 15 bar – Effect of HM_{wS}</i>						
M-02 ^a	27	15	1036	31	-	171
M-03 ^a	19	15	999	35	-	182
M-04 ^b	22	15	729	27	181	-
M-05 ^b	24	15	760	23	155	-
M-06 ^b	31	15	1027	58	368	-
M-07 ^b	31	15	1002	62	379	-
M-08 ^{a,b}	29	15	962	56	360	277
M-09 ^a	30	15	986	53	-	266
M-10 ^a	33	15	880	54	-	250
M-11 ^b	21	15	886	54	428	-
<i>Membrane performance at 15 bar – Effect of MWNTs loading</i>						
M-12 ^a	32	15	986	54	-	283
M-13 ^a	33	15	1014	54	-	265
<i>Membrane performance at 28 bar</i>						
M-14 ^b	25	28	224	16	139	-
M-15 ^b	33	28 ^b	326	15	147	-
M-16 ^b	33	28 ^b	445	13	128	-

^a Feed gas composition: 20% CO₂, 59.8% CH₄, and 20.2% H₂ (dry basis).

^b Feed gas composition: 20% CO₂, 40% N₂, and 40% H₂ (dry basis).

Sweep gas: argon.

Other operating conditions: temperature = 107 °C, dry gas flow rates = 60/30 cm³/min (feed/sweep), sweep pressure = 1.1 bar, RH = 59.2%/47.4% (feed/sweep) at the feed pressure of 2 bar, and RH = 100%/72.5% (feed/sweep) at the feed pressures of 15 and 28 bar.

Table 3. Gas transport results of membranes tested at various temperatures of 103–121 °C.

Sample	T	RH		CO ₂ Perm	CO ₂ /H ₂	CO ₂ /N ₂	CO ₂ /CH ₄
	(°C)	(Feed)	(Sweep)	(Barrer)	-	-	-
M-11	103	100%	86.3%	691	32	225	-
	105	100%	86.2%	817	47	370	-
	106	100%	77.8%	882	52	403	-
	107	100%	72.5%	886	54	428	-
	110	100%	67.9%	828	53	451	-
M-10	107	100%	72.5%	880	54	-	250
	114	100%	57.2%	583	50	-	242
	121	100%	45.6%	432	48	-	251

Feed gas composition for M-10: 20% CO₂, 59.8% CH₄, and 20.2% H₂ (dry basis).

Feed gas composition for M-11: 20% CO₂, 40% N₂, and 40% H₂ (dry basis).

Sweep gas: argon.

Other operating conditions: pressures = 15/1.1 bar (feed/sweep), dry gas flow rates of 60/30 cm³/min (feed/sweep), and RH = 100%/72.5% (feed/sweep).

Table 4. Proposed parameters for the facilitated transport model developed by Nobel et al. [25].

α	K	D_{AB}	k_r	$P_{CO_2}^{SD}$
-	-	(cm ² /s)	(1/s)	(Barrer)
15 [54]	5 [54]	3×10 ⁻⁵ [55]	110 [56,57]	150 [58,59]

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Fig. 1. Schematic of the two-step mechanism for MWNT surface modification.

Fig. 2. FTIR spectra of (a) raw MWNTs, (b) AT-MWNTs, and (c) AF-MWNTs.

Fig. 3. CO₂/H₂ selectivity as a function of high molecular weight species content in solid membrane composition using different polyamines as fixed-site carriers: (●) as-received Lupamin[®] 9095, (▲) purified Lupamin[®] 9095, and (■) PAA. Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed/sweep), dry gas flow rates = 60/30 cm³/min (feed/sweep), RH = 100%/72.5% (feed/sweep).

Fig. 4. CO₂/CH₄ separation performance of the MMMs developed by this work and tested at 2 bar (●, Sample M-01) and 15 bar (▲, M-08, M-09, M-10). The solid lines represent Robeson's updated upper bound [12]. Other operating conditions: temperature = 107 °C, sweep pressure = 1.1 bar, dry gas flow rates = 60/30 cm³/min (feed/sweep); at 2 bar, RH = 59.2%/47.4% (feed/sweep); at 15 bar, RH = 100%/72.5% (feed/sweep).

Fig. 5. Effects of feed pressure on CO₂ permeability (▲), CO₂/N₂ selectivity (○), and CO₂/H₂ selectivity (□). Operating conditions are listed in Table 2.

Fig. 6. Effects of AF-MWNT loading on CO₂ permeability (▲), CO₂/CH₄ selectivity (○), and CO₂/H₂ selectivity (□). Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed/sweep), dry gas flow rates = 60/30 cm³/min (feed/sweep), RH = 100%/72.5% (feed/sweep).

Fig. 7. Effects of sweep-side RH on the CO₂ permeability (▲), CO₂/CH₄ selectivity (○), and CO₂/H₂ selectivity (□) of the membrane M-09. Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed/sweep), dry gas flow rates = 60/30 cm³/min (feed/sweep), RH = 100%/72.5% (feed/sweep).

Fig. 8. Effects of operating temperature on membrane separation performances at a feed pressure of 15 bar: (1) CO₂ permeabilities of the membranes M-10 (▲) and M-11 (●); (2)

CO₂/H₂ selectivities of M-10 (Δ) and M-11 (○). Other operating conditions are listed in Table 3.

Fig. 9. Effects of selective layer thickness on CO₂ permeability (▲) and CO₂ permeance (◇).

The solid and dash lines are calculated using Noble's mathematical model [25]. Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed pressure), dry gas flow rates = 60/30 cm³/min (feed/sweep), RH=100%/72.5% (feed/sweep).

Fig. 10. Effects of selective layer thickness on CO₂/CH₄ selectivity (●) and CO₂/H₂ selectivity (□). The solid and dash lines are calculated using Noble's mathematical Model [25]. Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed pressure), dry gas flow rates = 60/30 cm³/min (feed/sweep), RH=100%/72.5% (feed/sweep).

Fig. 1. Schematic of the two-step mechanism for MWNT surface modification.

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Fig. 3. CO_2/H_2 selectivity as a function of high molecular weight species content in solid membrane composition using different polyamines as fixed-site carriers: (●) as-received Lupamin® 9095, (▲) purified Lupamin® 9095, and (■) PAA. Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed/sweep), dry gas flow rates = 60/30 cm^3/min (feed/sweep), RH = 100%/72.5% (feed/sweep).

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Fig. 9. Effects of selective layer thickness on CO_2 permeability ($\blacktriangle$) and CO_2 permeance ($\diamond$). The solid and dash lines are calculated using Noble's mathematical model [25]. Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed pressure), dry gas flow rates = 60/30 cm^3/min (feed/sweep), RH=100%/72.5% (feed/sweep).

Fig. 10. Effects of selective layer thickness on CO₂/CH₄ selectivity (●) and CO₂/H₂ selectivity (□). The solid and dash lines are calculated using Noble's mathematical Model [25]. Operating conditions: temperature = 107 °C, pressures = 15/1.1 bar (feed pressure), dry gas flow rates = 60/30 cm³/min (feed/sweep), RH=100%/72.5% (feed/sweep).