Polyamidoamine-facilitated Poly (ethylene glycol)/Ionic Liquid based Pressure Swing Membrane Absorption Process for CO₂ Removal from Shifted Syngas

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ABSTRACT: Pre-combustion capture of CO₂ from shifted syngas is a major route for carbon capture and sequestration from integrated gasification combined cycle for coal as the fuel. Conventional Selexol absorption-based processes involve cooling the gas to near-ambient temperature. A novel cyclic 5-valve pressure swing membrane absorption (PSMAB) process is being developed for CO₂ removal from lower-temperature shifted syngas at ~ 100°C in hollow-fiber membrane contactors using ionic liquid (IL) absorbent, 1-butyl-3-methyl-imidazolium dicyanamide ([bmim][DCA]). Separation performance is considerably enhanced by adding nonvolatile polyamidoamine (PAMAM) dendrimer Generation 0 to the IL at higher temperatures for a 40% CO₂, 60% He (surrogate for H₂) feed. Absorption performance in the cyclic process depends on selective sorption and other absorbent properties especially viscosity and hollow-fiber membrane contactor module design employing microporous hydrophobized polyether ether ketone (PEEK) hollow fiber-based membranes. Equilibrium CO₂ solubility and CO₂-He selectivity for IL, [bmim][DCA], has been compared with those for poly(ethylene glycol) (PEG) 400 which yields improved equilibrium CO₂-He selectivity and CO₂ absorption with/without 20 wt% PAMAM dendrimer over the temperature range 50-100°C. The PSMAB process separation performance has been explored using PEG 400-based absorbent in two hollow-fiber membrane contactor modules with improved designs in series at temperatures up to 100°C and feed-gas pressures up to 1720 kPag. This performance has been compared with that of the system using IL, [bmim][DCA]. The dendrimer-IL system performance for two modules-in-series with reduced dead volume considerably enhanced separation yielding >95% CO₂ in the CO₂-enriched product; further this performance exceeded easily that of the PEG 400-based system.

Keywords: Membrane contactor; Reactive gas absorption; Pressure swing membrane absorption; Hollow fiber membrane; Ionic liquid; PEG 400

1. Introduction

Many investigations and analyses have suggested that emissions of anthropogenic CO₂, a greenhouse gas (GHG), contributes heavily to global warming resulting from emissions of various GHGs [1]. To mitigate this problem, CO₂ removal and its subsequent sequestration is being widely studied under the general heading, carbon dioxide capture and storage (CCS) [2, 3]. Flue gas from coal-fired especially pulverized coal-fired power plants is one of the primary sources of CO₂ emissions. Due to the low partial pressure of CO₂ *in the flue gas*, economic capture of CO₂ from flue gas is demanding. On the other hand, precombustion capture of CO₂ from shifted syngas may be considered somewhat easier since CO₂ is present at a much higher partial pressure. However this gas obtained via integrated gasification combined cycle (IGCC) for coal comes in at a high temperature and pressure *which creates its own problems*.

Conventionally, the post-shift reactor synthesis gas is cooled, humidified and expanded to recover some electrical energy and then sent to Claus and Selexol units for H₂S removal and CO₂ separation by absorption respectively [4]. The separated CO₂ is then conditioned and compressed for sequestration. *The Selexol process for CO₂ absorption is operated at near ambient condition of ~ 38°C. In the Benfield process based on aqueous solution of hot potassium carbonate with an activator, the CO₂ absorber is operated at 75°C whereas the stripper operates at temperatures around 115°C. Therefore considerable additional heat input is needed for stripping.*

The processes of chemical, physical or hybrid absorption, adsorption, membranes separation or cryogenic separation are usually applied for separation of CO₂ contained in a gas mixture. However most of these processes will involve cooling down of the gas stream from the

high temperatures of shifted syngas. A separation process wherein the post-shift reactor gas stream is not cooled down or partially cooled down would be of interest. The low temperature (L-T) water gas shift reactor product stream is likely to be available at ~20 atm and around 200 °C. If CO₂ from this stream is to be absorbed for example in a liquid absorbent, the absorbent must be thermally stable and essentially nonvolatile. Further it must have substantial CO₂-selectivity over H₂ and any other impurities present (e.g., CO). The post L-T water gas shift reactor product stream will also have significant moisture. Absorbents which function without any need for H₂O as well as those which require H₂O for selective CO₂ absorption are of interest.

Ionic liquids are one such class of absorbents having negligible volatility and significant CO₂ selectivity over gases like N₂, H₂. For the ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆], Yokozeki and Shiflett (2007) [5] among others have demonstrated at around room and lower temperatures a solubility selectivity of CO₂ over H₂ of as much as 30-300 at H₂ partial pressures of 0.5-3 MPa. Chau et al. [6] determined the solubility of the individual gases CO₂ and He and the solubility selectivity of CO₂ over He over the temperature range of 50-100°C and a pressure of up to 1.40 MPa for the ionic liquid 1-butyl-3-methyl-imidazolium dicyanamide ([bmim] [DCA]); He was used since in the separation process studied next He was used as a surrogate for H₂.

Ionic liquid based membranes immobilized in the pores of a membrane to create a supported liquid membrane (SLM) have been used for selective CO₂ permeation at temperatures as high as 125°C [7]. These membranes suffer from the fact that diffusivity selectivity favors the smaller molecule He or H₂ whereas CO₂ is highly favored by solubility selectivity. Task specific ionic liquids having functional groups which can form complexes with CO₂ have been synthesized and used as facilitated supported liquid membrane (FSLM) (Myers et al., [8]); the

CO₂/H₂ selectivity achieved by such a FSLM reached up to 10-20 at a temperature of ~85°C. Albo et al. [9] studied CO₂ capture in the ionic liquid [emim][EtSO₄] using a polypropylene (PP) hollow fiber membrane contactor at ambient temperatures for simulated flue gas. Gomez-Coma et al. [10] studied the influence of temperature in CO₂ absorption in membrane contactors for two ionic liquids, [emim][EtSO₄] and [emim][Ac]. Mulukutla et al. [11] investigated reactive absorption of CO₂ in the ionic liquid [bmim][DCA] containing 20 wt% polyamidoamine (PAMAM) dendrimer Gen0 from simulated flue gas and its regeneration by employing rectangular cross-flow hollow fiber membrane modules made of porous PP hollow fibers having a porous plasma polymerized fluorosiloxane coating on the outside diameter.

Ionic liquids are expensive for larger-scale utilization. One wonders whether there are other less expensive substitutes. Depending on the range of temperatures, the viscous oligomeric liquid, polyethylene glycol (PEG) 400, may be an effective inexpensive substitute for ionic liquids. The compound PEG 400 is not very stable in air at > 80°C; however in the absence of oxidation agents, no degradation is expected (Han et al. [12]). The post-shift reactor syngas is essentially devoid of O₂. It is necessary to find out the solubility selectivity of PEG 400 for CO₂ over other gases from which it has to be separated over the temperature range of interest. It is known that the solubility selectivity of ionic liquids for CO₂ decreases strongly as temperature increases. To enhance the solubility selectivity, one can add nonvolatile amines e.g., PAMAM dendrimer Gen 0 to the ionic liquid [6]. The enhanced CO₂ selectivity of PEG 400 containing some PAMAM dendrimer is also of interest. We report results of solubility of CO₂ and He in such absorbents here and compare the values with those based on the ionic liquid [bmim][DCA].

In conventional absorption processes, the absorbent is circulated between the absorber and the stripper (for regeneration). Essentially nonvolatile absorbents for CO₂ such as ionic

liquids and PEG 400 are quite viscous. The viscosity is increased considerably when PAMAM dendrimer Gen 0 is added at the level of 10-30 wt%. The viscosity does get reduced at higher temperatures. However if membrane contactors are to be used with microporous hollow fiber membranes highly packed in the contactor to provide a large gas-liquid interfacial area per unit device volume, the pressure drop with a flowing absorbent would be considerable; maintaining nondispersive operation with microporous membranes will be challenging especially when the gas pressures are quite high.

To that end, we recently developed a cyclic pressure swing membrane absorption (PSMAB) process in which the absorbent is stationary on the shell-side of a microporous hydrophobic hollow fiber membrane device. The feed gas at a high pressure is periodically introduced into the bore of hollow fiber membranes in the device. The operational configurations employed here have some similarities to pressure swing adsorption (PSA) processes as if we were working with adsorbents. The basic concepts of the PSMAB process have been illustrated in the following references: Jie et al. [13], Jie et al. [14], Chau et al. [15].

Using this approach, the performance of the PSMAB process has been investigated here using the absorbent PEG 400 with and without 20 wt% PAMAM dendrimer Gen 0 for the separation of a CO₂-He mixture over the range of 25-100°C and 690-1720 kPag feed gas pressure with He acting as a surrogate for H₂. Data for [bmim][DCA] with and without 20wt% PAMAM dendrimer Generation 0 have also been provided for comparison. The major difference between these results and the system used in [14] for [bmim][DCA] based absorbent is that the membrane area has been increased here by having two larger membrane modules in series. Further the dead volume in the headers of both modules has been reduced.

Conventional PSA processes are very efficient in purifying the less-adsorbed species. On the other hand, conventional PSA processes are not very efficient in purifying the most-adsorbed species, the so-called heavy product [16]. A major reason for this is the significant volume of feed gas left in the void volume of a saturated bed. More complex PSA system designs are adopted to develop a stream containing the most-adsorbed species with high purity [17, 18]. Here in the PSMAB process, the species corresponding to the most-adsorbed species in PSA is CO₂. However, by having a reversibly chemically reactive system in the absorbent, the purity of the absorbed species is enhanced considerably. Such an approach is also being utilized in PSA-based CO₂ recovery research [19]. In addition, the void volume fraction corresponding to the fiber bore side volume is significantly lower than that in PSA systems.

For CO₂ removal it has been suggested that "Three main approaches are mainly under study: i) non-dispersive absorption using porous membranes; ii) gas permeation; and, iii) supported liquid membranes"[20]. We suggest here that a fourth approach involves employing non-dispersive absorption as well as non-dispersive stripping via a cyclic process using the same porous membrane used for absorption.

2. Materials and Methods

2.1. Materials and chemicals

Polyethylene Glycol 400 (PEG-400) was purchased from Chem World (Roswell, GA, USA) and used as received. PAMAM dendrimer (Gen 0) (Dendritech, Midland, MI, USA) was supplied in a methanol solution containing 64.05 wt% dendrimer. Pure PAMAM dendrimer Generation 0 was obtained by subjecting the solution to vacuum at ~ 60°C for several days. Ionic liquid (IL), [bmim][DCA], (EMD Chemicals, Philadelphia, PA, USA) was used as received. A

gas mixture containing 40.67% CO₂, helium balance (Air Gas, Salem, NH, USA) was employed as the shifted syngas.

Details of the membrane modules built of microporous hydrophobized polyether ether ketone (PEEK) hollow fibers membranes (Porogen, Woburn, MA) are provided in Table 1. These modules are identified as PEEK-L-III. More details of such a module vis-à-vis other modules using similar hollow fibers are provided in [14]. Hollow Teflon balls having a diameter of *0.3175 cm* were obtained from Engineering Laboratories (Oakland, NJ, USA).

2.2 Method: PSMAB process description based on 5-valves

It is useful to illustrate briefly the basic operational and device concepts for PSMAB as illustrated in Figures 1a and 1b. The pressure swing membrane absorption process utilizes 5 on-off valves around the membrane modules. The stepwise process is carried out as follows in any given cycle.

Fresh feed gas in: Fresh feed gas humidified or otherwise enters the tube-side of the hollow fiber membrane modules through an open valve 1 at a high pressure for a short period of time. The tube-side pressure rises up to the feed gas pressure quickly. This step usually lasts for 5-10 s. The four other valves are closed at this time. (Step 1)

Feed gas absorption: Valve 1 is closed after the feed gas introduction; gas absorption into the shell-side absorbent takes place. This step continues for 30-60 s. We need to mention here that there is gas absorption going on as the fresh feed gas is introduced into the membrane modules as well in the earlier step. As a result the gas located at the furthest point from the feed gas entrance is purer in helium than at any other locations since the absorbent is CO₂-selective. (Step 2)

He-rich product stream released: Valve 3 is now opened for 1-10 s and a He-rich gas stream is withdrawn. All other valves remain closed at this time. (Step 3)

Middle part gas withdrawal: Valve 4 is now opened for 2-5 s while all other valves are closed. A certain amount of relatively He-rich gas is withdrawn from the modules into a middle part gas reservoir. (Step 4)

CO₂-rich product withdrawal: Valve 2 is now opened to a low pressure for 30-60 s to allow desorption of the absorbed CO₂ and produce a CO₂-rich product stream which flows out. All other valves remain closed. (Step 5)

Recycle middle part gas to feed location: With all valves remaining closed, valve 5 is opened for 2-5 s and the middle part gas is recycled into the tube-side of the membrane module to become feed gas coming in at a lower pressure. (Step 6)

With this step, one complete cycle of the six-step cycle is completed. This step is followed by introduction of the high pressure fresh feed gas into the tube-side of the membrane module. Figure 1b shows the tube-side pressure conditions for the first cycle. From the second cycle onwards, the step of recycling middle part gas stream is part of the feed gas introduction-based pressure rise in the tube-side of the membrane module.

This 5-valve based PSMAB system was first proposed by Jie et al. [13]. The cycle time varies between 75 to 150 s; a typical distribution of cycle time for each step in second for the 6 steps is as follows: 10; 60; 1; 3; 60; 2. Generally one small membrane module was used to study the process [13,14]. Here we have two membrane modules to increase the membrane surface area. In a given experiment, there will be hundreds of cycles implemented without any break.

After the gas absorption step, the gas mixture in the tube-side of the module may be considered to consist of three parts: He-rich product, middle part gas and the feed end product. After the

He-rich product is withdrawn, withdrawal of the middle part gas leads to a better CO₂-rich product stream resulting from desorption of the highly CO₂-enriched absorbate. Recycling the middle part gas into the feed side end of the tube side before the fresh feed gas comes in provides an opportunity to have a somewhat He-enriched stream mix with the fresh feed gas.

2.3 Experimental setup and procedure

The solubility of pure CO₂ and pure He in two absorbents, pure PEG 400 and PEG 400 containing 20 wt% dendrimer with and without moisture was determined in a pressure-decay dual-transducer apparatus described in detail by Chau et al.[6]. The measurements were made in the temperature range of 50-100°C at pressures of up to 1.40 MPa. The apparatus was located in an oven (Model PH-202, ESPEC North America, Hudsonville, MI, USA).

For the experimental setup and procedure employed for the PSMAB studies, the readers should refer to Jie et al. [13] and Jie et al.[14] for more detailed description beyond that provided below.

Before any PSMAB experiments were done with any membrane module, the breakthrough pressures of the module were determined at room temperature using successively the following liquids: water, PEG 400, 20 wt% PAMAM in PEG 400. Tests were conducted earlier also with the IL [14]. Any test liquid used to fill up the shell side of the membrane module was pressurized by N₂ gas from a cylinder. To detect any breakthrough of the test liquid through the pores present on the outside surface of the hollow fiber membrane, N₂ gas was passed through the tube-side of the hollow fibers. The N₂ gas pressure at which any leaked test liquid could be detected from the tube side was defined as the breakthrough pressure.

Figure 2a illustrates the experimental setup used to study the performance of the PSMAB process with two hollow fiber membrane modules in series. Figure 2b provides a larger scale

view of the hollow fiber membrane module used and identifies various sections of the hollow fiber module with the Teflon balls reducing the dead volume in the tube-side headers. The PEG 400 based absorbent (or the ionic liquid [bmim][DCA]-based absorbent) was introduced from a reservoir into the shell side of the membrane module by gas pressure from a N₂ cylinder. This N₂ cylinder pressure was always maintained at ~140 kPag higher than the feed gas pressure employed in a given experiment to prevent bubbling of the gas into the absorbent liquid.

The feed gas used was 40.67% CO₂, balance He. This gas mixture from a cylinder was first bubbled into a water bath if the feed gas was to be humidified. The humidified feed gas was introduced into the tube side of the membrane module through valve 1. The feed gas got absorbed into the absorbent or desorbed out of the absorbent at the mouth of the micropores on the outside surface of the hollow fibers. A water pump (HP model 1100, Waldbronn, Germany) was used to inject water into the system. Five pneumatically-driven on-off valves numbered 1 to 5 were closed or opened at precise time intervals in a given absorption-desorption cycle. A Programmable Logic Controller (PLC) installed by Pneumatic (Quakertown, PA, USA) was employed to control the valves. A vacuum pump beyond the valve 2 in the CO₂-rich product withdrawal line was employed for withdrawing the CO₂-rich product. This experimental setup was placed inside an oven (Model PV-222; Espec Corp. Hudsonville, MI, USA) to maintain the test temperature.

The PSMAB system produced stable results after the first 5-10 cycles. The data reported were taken after at least 30 cycles; the tests were repeated three times. To determine real-time concentration fluctuations of CO₂ in the CO₂-rich and He-rich product streams, a Quantek Model 906 CO₂ Analyzer (Grafton, MA, USA) was utilized. The compositions were also analyzed sometimes by a HP 5890A GC (Santa Clara, CA, USA) using a Hayesep D 100/120 packed

column (Alltech, Deerfield, IL, USA). The oven temperature was 100°C; the TCD temperature was 125°C. The carrier gas was helium.

To monitor and understand the gas absorption process, a pressure transducer was directly connected to the feed gas inlet location of the tube-side of the membrane module next and between valves 1 and 2 inside the oven. This arrangement consisted of a pressure transducer (Model PX32B1-300GV, Omegadyne, Sunbury, OH, USA), an assembly cable (Model CA-6TE24-010-PX32) and a universal input Ethernet (Model DP41-B-EI). Detailed recording of the change in gas pressure with time allowed studying the gas absorption process in the membrane module.

3. Results and Discussion

3.1. Solubility and solubility selectivity of CO₂/He in PEG 400-based absorbents

The values of Henry's law constant for pure CO₂ and pure He in the absorbent pure PEG 400 are reported in Table 2 at four different temperatures, 50°C, 80°C, 90°C and 100°C. Literature value of Henry's law constant at 50°C for CO₂ in PEG 400 (Li et al., [21]) shown in the last column is very close to the value experimentally obtained at 50°C. As expected CO₂ solubility decreases with an increase in temperature. However the solubility of He increases somewhat with temperature. Such a behavior was also observed earlier with the ionic liquid [bmim][DCA] [6]; the reason for such a behavior with low solubility gases such as, He, H₂, N₂ has been discussed earlier [6]. One important item to note is that CO₂ solubility in PEG 400 is higher than that in [bmim][DCA] [6].

Table 3 provides the values of Pseudo-Henry's law constants for both CO₂ and He in PEG 400 containing 20 wt% PAMAM dendrimer Generation 0 at four different temperatures, 50°C, 80°C, 90°C and 100°C. The Pseudo-Henry's law constant [6] has been defined as the value

of the slope of the curve of the gas partial pressure vs. the mole fraction of the species in the liquid as the mole fraction tends to zero. Note that there are two sets of data: dry gas; significant moisture is present. As expected, the CO₂ solubility increases significantly around 2.0-2.6 times due to chemical reactions with the primary amines in the case of dry gases. The increase is significantly larger when moisture is present in the system since the tertiary amines are activated in addition by moisture. Since each PAMAM dendrimer molecule has four primary amines and two tertiary amines, the following reactions are expected to occur ([6], Mulukutla et al. [22]):

References [6] and Mulukutla et al. [22] have provided spectroscopic justifications for the species observed in such reactions with the dendrimers in [bmim][DCA]. Since He does not participate in the reactions with the amine groups, there is a very limited effect of the presence of the dendrimer molecules on He solubility.

It is useful to provide a perspective on the relative values of the CO₂-He selectivity at two different temperatures for the two different absorbents, PEG 400 and [bmim][DCA], with and without PAMAM dendrimer Gen 0; further both cases of dry gas and moisture present are considered. The data for [bmim][DCA] plotted here were obtained from the earlier study [6]. Figures 3 and 4 provide the data respectively for 50°C and 100°C. At a comparable level of PAMAM addition (20 wt%) or without any PAMAM addition, PEG 400 appears to have a higher solubility selectivity than [bmim][DCA]. Here the solubility selectivity of CO₂ over He is defined as the ratio of the Pseudo-Henry's law constant for He divided by that for CO₂. The data clearly show two behaviors: Higher temperature reduces the CO₂ solubility and CO₂/He selectivity in both absorbents; moisture enhances CO₂ solubility and CO₂/He

selectivity considerably in both absorbents. Such data will facilitate understanding of some of the observed behaviors in the PSMAB process results considered later.

3.2. Breakthrough pressure of microporous hollow fiber membranes

In any given PSMAB experiment, the tube-side pressure varies all the way from the high feed gas pressure to less than atmospheric pressure during CO₂-rich product withdrawal. The liquid absorbent pressure must be slightly larger than the high feed gas pressure to prevent gas bubbling into the absorbent liquid during feed gas introduction. This high liquid pressure should not however allow the liquid to break through the pore into the gas phase when the tube-side pressure is drastically reduced during some other parts of the cycle. Since the highest feed gas pressure studied is 1720 kPag and the absorbent liquid pressure has to be somewhat larger, therefore the absorbent liquid must not breakthrough at pressures somewhat larger than 1720 kPag. The test results *obtained* indicate that for all three liquids *studied* namely, water, PEG 400 and PEG 400 containing 20 wt% dendrimer, there was no breakthrough at 2070 kPag. The breakthrough pressure therefore must be higher. In an earlier paper [14], the breakthrough pressure for [bmim][DCA] for the same hollow fibers was observed to be higher than 1720 kPag.

3.3. Tube-side pressure profile in a given cycle

It is highly illustrative to plot the state of the tube-side pressure in the hollow fiber in a stepwise fashion over the six-step process in a given cycle of the PSMAB process. Figure 5 shows the pressures at the beginning and end of each step in the 6-step process in any cycle for the case where the feed gas came in at a pressure of 1720 kPag for the PEG 400 system with 20 wt% dendrimer. The data correspond to a feed gas temperature of 75°C. The durations of various parts of the cycle in second are indicated in an inset in the figure where x indicates the duration of the middle part gas withdrawal which had two values, 2 and 3 s. Correspondingly the

percentage of CO₂ in the CO₂-rich product stream increased from 92.1% to 94.1%; this was achieved since a larger amount of He-rich fraction left in the module end opposite to the feed introduction section was withdrawn as the middle part gas; this allowed an increase in CO₂ concentration during CO₂ desorption and CO₂-rich product withdrawal.

3.4 The total gas absorption behavior over an extended duration for the absorption step

Previous studies [13, 14, 15] indicated how important the feed gas absorption step is in the PSMAB process since most gas-liquid contact and selective absorption take place during this part of the non-dispersive gas-liquid contact. Although 60 s was used for the feed gas absorption step in all studies reported here, a special experiment was conducted where duration of this step was extended to 900 s with dry feed gas at 100°C and 1030 kPag pressure. Both absorbents, PEG 400 and [bmim][DCA], were studied; both contained 20 wt% PAMAM dendrimer Gen 0. Figure 6 illustrates the results.

It appears that the pressure drop encountered initially over the first 120 s was somewhat larger for [bmim][DCA]. However as time progressed, the pressure drop for the PEG 400-based system became significantly larger indicating larger amount of absorption. The reason for this observed behavior is as follows. Although the viscosity of the ionic liquid, [bmim][DCA], is high (e.g., at 20°C, 33.15 mPa.s), it is significantly lower than that of PEG 400 (e.g., at 20°C, 120 mPa.s); this relative behavior is not changed by the addition of the dendrimer which increases the viscosity considerably. The rate of gas absorption is influenced strongly by the value of the gas diffusion coefficient which is approximately inversely proportional to the liquid viscosity. Therefore, the initial rate of gas absorption is higher with the ionic liquid-based system. However, as time progresses, the higher CO₂ solubility of the PEG 400-based system takes over leading to the significantly larger pressure drop as the system approaches equilibrium and the

decrease in gas pressure starts flattening out. It is expected that such differences in the initial time absorption behavior will be significantly reduced in the presence of moisture which will reduce the absorbent viscosity considerably. Note that only one PEEK-L-III module was used for this particular experiment without any Teflon balls in the tube-side headers.

3.5. Separation behavior of the PSMAB process for pure PEG 400 absorbent

It has been pointed out earlier [13] that the membrane modules used had considerable amount of dead volume in the tube-side header section and the potted tube-sheet section. The header section dead volume was reduced significantly by filling it up with hollow spherical Teflon balls in a few experiments [14]. Following that approach, two such modules were put in series (as shown in Figure 2a) and employed to study the performance of the 5-valve PSMAB process for pure PEG 400 as the absorbent. The results are shown in *Figure 7*. It employed a step time distribution for the six steps in the PSMAB process as follows where the unit of time is second-- 10:60:2:2:60:2.

Figure 7 clearly shows that for a given feed gas temperature in the range of 25-75°C, as the feed gas pressure increases from 690 kPag to 1380 kPag, the composition of the CO₂-rich gas product is significantly enhanced in CO₂. This is because more CO₂ is absorbed at a higher feed pressure leading to better CO₂-quality in the CO₂-enriched product stream. On the other hand, as the feed gas temperature is increased from 25 to 75°C, the composition of the CO₂-rich gas suffers a decrease in terms of CO₂ since as seen earlier CO₂-He selectivity and CO₂ solubility are adversely affected by an increase in temperature. For the He-rich product stream, any increase in feed gas pressure leads to a product stream with increasing CO₂. Increase in temperature at a given feed gas pressure leads to a similar deterioration in performance.

Figure 8 illustrates the results from a somewhat comparable situation with the pure ionic liquid [bmim][DCA] in one PEEK-L-III module without any Teflon balls in the headers. One observes a somewhat better performance in terms of the CO₂ composition in both product streams compared to those for the PEG 400 absorbent. For example at *1380* kPag and 75°C the CO₂-rich stream has 87.5% CO₂ with the pure ionic liquid compared to 74.4% CO₂ for pure PEG 400 (the latter with two modules in series). Although the difference is significantly lower for the He-rich stream, nonetheless, the ionic liquid-based system performs better. This is primarily due to the higher viscosity of the PEG 400-based system.

3.6. PSMAB Process Performance at Higher Temperatures in the Presence of 20 wt% PAMAM Dendrimer Gen 0 in Mixed Absorbents

Figure 9 shows the structure of the PAMAM dendrimer Gen 0 used. The primary amines and the tertiary amines react with CO₂ via the equations (1) and (2) respectively. *Figure 10* illustrates the PSMAB process performance over the temperature range of 25-75°C and a pressure range of *690-1720* kPag when the absorbent PEG 400 has 20 wt% PAMAM dendrimer Gen 0 dissolved in it. It appears that as the temperature goes up from 25 to 75°C, the quality of both product streams improve with the CO₂-rich product stream going up to 93.8% CO₂. This merely reflects the decreasing viscosity of the absorbent and therefore increasing absorption of CO₂ leading to a better separation. The performance however deteriorates when the temperature goes up to 100°C as will be shown below.

Figure 11 illustrates the effect of a change in the middle part gas withdrawal time from 2 s (*Figure 11 a*) to 3 s (*Figure 11b*) in the PSMAB cycle for the PEG 400 based absorbent (containing 20 wt% dendrimer) at 75°C over a feed pressure range of *690-1720 kPag*; data are provided for 100°C for the 3 s time also. It appears that the increase in the middle part gas withdrawal time *from 2 s to 3 s* leads to a significant enhancement in the purity of the two

streams especially the CO₂-rich stream; it goes up from 92.1% CO₂ to 94.1% CO₂. This results from removal from the tube-side of a more He-enriched stream leaving a more CO₂-containing stream which then gets mixed with the highly CO₂-rich stream resulting from desorption at a much lower pressure. However, *Figure 11* also shows that the performance deteriorates as the temperature goes up to 100°C.

Figure 12 provides the data for the IL-based system for the temperature range of 75-100°C and a pressure range of 1030-1720 kPag. At the highest pressure of 1720 kPag and temperature 100°C, the CO₂-rich product stream has a CO₂ content of 95.5%. This is the highest value achieved so far by this technique. It certainly meets the US Department of Energy (DOE) target of 95%+ CO₂ in the CO₂-rich product stream. This value is considerably larger than 89.7% CO₂ achieved with the PEG 400-based system per *Figure 11*.

If the residual dead volume in the headers of the membrane module is reduced further, this value will go up yielding an even more CO₂-enriched stream. Membrane module redesign is necessary to achieve such a goal. The module redesign should include much increased membrane surface area/per unit header volume which will reduce considerably the impact of any dead volume. It will also allow the use of a higher pressure withdrawal of this CO₂-enriched stream. *Figure 12* also indicates that the He-rich product stream had a CO₂ level of 19.7% at the highest feed gas temperature and pressure. To decrease this value to the level of 2-5% CO₂, longer module length is necessary; further minor modifications in the cycle design are warranted. That such a level is achievable has already been demonstrated under less demanding absorption conditions in earlier studies (Figure 5 in Jie et al. [13]). Therefore, module redesign, longer module length and very minor cycle-valve redesign in the PSMAB process will ensure

simultaneous achievement of the desired product purities at both ends of the membrane modules in series.

One of the advantages of PEG 400 is that it is quite inexpensive vis-à-vis the IL used. However, it is clear that the much higher viscosity of PEG 400 has an unfavorable impact on its mass transfer performance even though it has a higher equilibrium sorption of CO₂ and higher equilibrium CO₂/He selectivity compared with those for the IL used with and without the dendrimer. It would be useful to explore other inexpensive nonvolatile absorbents having lower viscosity.

Conventional pressure swing adsorption processes for gas separation are usually designed for producing a highly purified stream of the less adsorbed species. By introducing reactive absorbents, it has been shown here that the more highly absorbed species can be considerably purified as well via the PSMAB process. A further reduction in the dead volume in the headers and the tube-sheet would have enhanced the purity of the CO₂-rich stream still further.

4. Concluding Remarks

This work has investigated several aspects for further development of the new PSMAB process for separation of shifted syngas at lower temperatures of 75-100°C and at pressures of *1030-1720* kPag. The aspects of interest are: (1) Equilibrium sorption capacity of CO₂ and He and the sorption selectivity CO₂/He over 50-100°C for two absorbents PEG 400 and [bmim][DCA] with or without PAMAM dendrimer Gen 0 at the level of 20 wt% in the presence or absence of moisture; (2) Separation performance in terms of CO₂-rich stream purity when two membrane absorption modules are used in series with reduced header dead volumes in each module. The absorbent PEG 400 has higher equilibrium solubility of CO₂ vis-à-vis the IL [bmim][DCA] as well as higher CO₂/He absorption selectivity. These conclusions are valid in the presence or absence of 20 wt% dendrimer Gen 0 with or without moisture.

However, considerably higher viscosity of PEG 400 reduces the rate of absorption of CO₂ leading to poorer mass transfer performance over shorter time periods compared to those with the IL. Since the PSMAB process operates with short time steps in a given cycle, higher sorption capabilities must be accompanied by higher mass transfer performance. As a result the separation performance of the PSMAB process in terms of the purity of CO₂ in the CO₂-rich product is significantly poorer for the PEG 400-based systems. For the IL-based system containing 20 wt% dendrimer, under feed gas conditions of 100°C and 1720 kPag, the purity of the CO₂-rich product stream has been increased to 95.5% CO₂ when two membrane modules having reduced dead volumes in the module headers are used in series. Further modifications are suggested to achieve simultaneously much lower CO₂ concentration in the He-rich product stream. These conclusions provide useful guidelines for separation of any binary gas mixture by the PSMAB process if CO₂ is replaced by the more strongly absorbed species.

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GRAPHICAL ABSTRACT

Pressure Change Profile in the Hollow Fiber Membrane Lumen for Different Steps of the PSMAB Process for CO₂-He Feed Gas at 100°C and 1724 kPag

Table 1. Dimensional Characteristics of the Membrane Modules for the PSMAB Process

Module ¹	OD/ID; cm	L; cm	Pore Size ² ; Å	VVF	Fiber Number	Surface area ³ ; cm ²	A/V; cm ⁻¹	Packing Density, %
PEEK-L-III ⁴	0.047/0.0272	41.0	~20	~0.4	908	5500	57.4	27.2

¹ OD: outer diameter of fiber; ID: inner diameter of fiber; L: effective fiber length; VVF: void volume fraction;

² Pore size of the outside surface; ³Based on outer diameter of fibers; ⁴ PEEK-L-III module has a packing density around 27.2% that was defined as the ratio between total fiber volume and the real volume they occupied (total fiber volume plus space between the fibers in the fiber strands wound helically in the module).

Table 2. Henry's Law Constants of Pure CO₂ and Pure He in PEG 400 at Different Temperatures

Absorbent liquid	Temperature (K)	Henry's law constant (bar)		Reference H _{CO2} * (bar)
		H _{CO2}	H _{He}	
PEG 400	323	65.0±3.0	791.0±7.0	56.6±1.2 @313K
	353	91.0±2.3	566±10	65.4±0.7@323K
	363	102 ±2.0	463±9.0	70.9±1.2 @333K
	373	110.0±5.0	361.0±5	

*Li et al. [21]

Table 3. Pseudo-Henry's Law Constants of Pure CO₂ and Pure He for 20 wt% Dendrimer in PEG 400 with and without Moisture at Different Temperatures

Absorbent liquids	Temperature (K)	Pseudo-Henry's law constant (bar)	
		H _{CO2}	H _{He}
20 wt% dendrimer in PEG 400	323	25.0±2.0	800.0±12.0
	353	41.0±2.0	575.0±13.0
	363	48.0±3.0	473.0±8.0
	373	56.0±2.0	376.0±7.0
20 wt% dendrimer in PEG 400 with moisture	323	18.0±2.0	812.0±11.0
	353	34.0±4.0	584.0±11.0
	363	42.0±3.0	495.0±9.0
	373	50.0±6.0	433.0±12.0

Figure captions

Figure 1. Schematic diagram of 5-valve pressure swing membrane absorption process: Left hand side, 5-valve controlling system; Right hand side, tube side pressure change within one cycle.

Figure 2. (a) Schematic diagram of pressure swing membrane absorption apparatus having two small membrane modules in series; (b) More details about the hollow fiber membrane module showing Teflon balls used in the tube-side headers to reduce the dead volume.

Figure 3. Solubility selectivity of CO₂/He in different absorbent liquids at 50°C; DCA is short for [bmim][DCA] i.e., 1-butyl-3-methylimidazolium dicyanamide; [bmim][DCA] data are from *reference* [6].

Figure 4. Solubility selectivity of CO₂/He in different absorbent liquids at 100°C; *DCA is short for [bmim][DCA] i.e., 1-butyl-3-methylimidazolium dicyanamide*; [bmim][DCA] data are from reference [6].

Figure 5. Pressure conditions during various steps of a 5-valve PSMAB cycle up to CO₂ product release step for operation with a 1724 kPag (250 psig) feed gas pressure at 75°C.

Figure 6. Pressure drop in tube side during 900 s absorption duration tests using two absorbents: PEG-400 and [bmim][DCA] each containing 20 wt% dendrimer; dry feed gas and one module used.

Figure 7. Product qualities at different temperatures and feed gas pressures for two PEEK-L-III modules in series with PEG 400 as absorbent for a 5-valve PSMAB System. Unless specified, the time in each step is as follows in second: 10:60:2:2:60:2.

Figure 8. Product qualities at different temperatures and feed pressures for one PEEK-L-III module with [bmim][DCA] as the liquid absorbent (No Teflon balls).

Figure 9. Structure of PAMAM dendrimer of generation 0.

Figure 10. Product qualities at different temperatures and feed pressures for two PEEK-L-III modules in series with 20 wt% dendrimer in PEG 400 as the liquid absorbent for a five-valve PSMAB System (PTFE balls used in the headers).

Figure 11. Effect of Middle Part Gas Withdrawal Time in the Cycle on Two Product Stream Qualities for Operation at Different Feed Gas Pressures and Temperatures with Two Membrane Modules in Series for PEG 400 system with 20 wt% dendrimer. (a) Cycle time details in second: 10; 60; 1; 2; 60; 2. (b) Cycle time details in second: 10; 60; 1; 3; 60; 2.

Figure 12. Product qualities at different temperatures and feed gas pressures for two PEEK-L-III modules in series with 20wt% Dendrimer in [bmim][DCA] as the liquid absorbent and both headers in each module filled with Teflon balls. Cycle time details in second: 10:60:2:2:60:2.

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