An experimental and modeling study of CO₂-selective membranes for IGCC syngas purification

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Abstract

In recent years, integrated gasification combined cycle (IGCC) technology has gained significant attention for large-scale power generation with carbon capture. In an IGCC power plant, the syngas is typically directed to the gas turbine (for power generation) after CO₂ and H₂S removal. This work describes the transport properties of the CO₂-selective polymeric facilitated transport membranes for syngas purification at different pressures (2 – 15 bar) and 107°C. These membranes contain amines as CO₂-carriers that are dispersed in a crosslinked polyvinylalcohol (PVA) matrix. Furthermore, a two-stage membrane process is proposed for CO₂ removal from syngas in an IGCC plant. A process modeling and cost-sensitivity analysis of the proposed two-stage membrane process was performed. The effects of feed pressure, temperature, membrane permeance, and selectivity on the overall increase in the cost of electricity (COE) were analyzed. An increase in the COE of 14 – 18% was estimated for 90% CO₂ removal and > 99% H₂ recovery using the two-stage membrane process in an IGCC power plant.

Keywords: CO₂-selective membrane; Permeance; Selectivity; IGCC; Pre-combustion carbon capture

1. Introduction

One third of the total CO₂ emissions come from the burning of coal as a fossil fuel [1]. Certainly, the CO₂ emissions from the coal-based power plants would play a dominant role in governing the global warming trends. Thus, there is an imminent need to restrict the CO₂ emissions from the coal-based power plants. There have been various studies focusing on comparing the integrated gasification combined cycle (IGCC) technology for power generation against the conventional pulverized coal (PC) and the oxy-fuel based combustion technologies. However, the development of carbon capture processes would govern the implementation of these technologies for the large-scale power generation [2,3].

In an IGCC power plant, coal or biomass is used to produce syngas (CO + H₂) by the gasification process. The syngas can be used as a feedstock for the production of value added chemicals or for the generation of electricity via the gas turbine or the fuel cell. Currently, there are some IGCC demonstration units but the technology has not been commercialized due to large capital cost for the gasification system and downstream syngas processing. However, it is economically more feasible to integrate a carbon capture unit with an IGCC power plant relative to a conventional PC-based power plant. Therefore, IGCC power plants that are integrated with carbon capture are potential favorable alternatives for large-scale power generation.

Figure 1 shows a process flow scheme of an IGCC power plant with carbon capture. Gasification is typically carried out at high pressures (>50 bar) and at high temperatures (>700°C). Coal is gasified in presence of steam and oxygen to produce syngas. The oxygen is separated from air using the air separation unit (ASU) prior to the gasifier. The syngas from the gasifier is sent through a syngas quencher for tar and particulate removal prior to a series of water-gas-shift (WGS) reactors. The syngas is then passed through the WGS reactors where the

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6 carbon monoxide through reacting with steam is converted to carbon dioxide and hydrogen. The
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8 CO₂ and H₂S are required to be separated from the WGS reactor product stream for H₂
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10 purification. The enriched H₂ stream is directed to the gas turbine for large-scale power
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12 generation. The H₂S separated from the syngas (using the Selexol[®] process) is directed to the
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14 Claus unit for the sulfur recovery, and the captured CO₂ is sent for sequestration purposes.
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19 Membrane separation, solvent absorption and solid adsorption are three well-known
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21 processes for CO₂ removal [4]. Solvent absorption, at high pressures as well as low pressures, is
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23 well-developed among the three processes. The U.S. Department of Energy (DOE) have
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25 presented an independent techno-economic assessment (in their baseline document [5]) of the
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27 solvent absorption technologies for CO₂ removal in an IGCC, pulverized coal (PC) and natural
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29 gas combined cycle (NGCC) power plants. The state-of-the-art amine absorption process has
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31 been considered for CO₂ removal from the flue gas (at ~1 psig with ~14% CO₂ content) in
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33 conventional PC power plants. Furthermore, a physical absorption based Selexol[®] process is
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35 considered for high-pressure CO₂ removal from syngas in an IGCC power plant. The presence
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37 of high pressure syngas and a higher CO₂ concentration (~35%) in the gas stream resulted in a
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39 lower cost to incorporate the CO₂ removal technology in an IGCC power plant as compared to
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41 the conventional PC power plant. The integration of state-of-the-art monoethanolamine process
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43 for CO₂ removal to a PC power plant resulted in approximately 86% increase in the cost of
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45 electricity (COE). On the other hand, the incorporation of the Selexol[®] process for carbon
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47 capture in an IGCC power plant resulted in about 39% increase in COE [5].
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56 Absorption and adsorption processes are energy-intensive with significant parasitic power
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58 consumption. The membrane technology is a cost-effective process for H₂ purification due to
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60 lower energy consumption, lower capital cost, and operational simplicity. In an IGCC power
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6 plant with carbon capture, CO₂ needs to be separated from a high pressure gasification stream. A
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8 high pressure would mean a larger driving force for the membrane based CO₂ separation.
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10 However, separating CO₂ molecules selectively over the smaller-size H₂ molecules (2.89 Å) at
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12 high pressures is a challenging task.
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16 This work demonstrates attractive transport performances of CO₂-selective polymeric
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18 facilitated transport membranes for syngas purification. Furthermore, a process modeling and a
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20 systematic cost-sensitivity study of a two-stage membrane process for CO₂ capture from syngas
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22 in an IGCC power plant was performed. The IGCC power plant with the General Electric
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24 Energy (GEE) gasifier and no carbon capture (Case 1 of the baseline DOE document) was
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26 considered as the base case for further reference [5].
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32 **2. Membranes for CO₂ Capture**

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35 A membrane process is considered in this work for separating CO₂ from syngas after the
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37 water-gas-shift reaction. The captured CO₂ is required to be recompressed for sequestration
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39 purposes. The enriched H₂ stream is sent to the gas turbine at high pressures (~ 32 bar) for
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41 power generation [5]. Since all the respective enriched gas streams (H₂-rich gas stream, captured
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43 CO₂ and H₂S streams) would be processed further at high pressures, it would be more
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45 energetically favorable to operate the CO₂ and H₂S removal units at high pressures.
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50 There are various CO₂- and H₂-selective membranes published in the literature for syngas
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52 purification at different pressures [6-10]. Inorganic palladium based membranes are reported for
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54 permeating H₂ at an almost infinite selectivity [4]. However, it suffers from severe sulfur
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56 poisoning (on exposure to H₂S) along with hydrogen embrittlement [11]. Moreover, it is
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58 difficult to scale up the fabrication of the state-of-the-art palladium membranes that could be
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5 rolled into large robust modules for practical applications. On the other hand, there are
6 considerable developments in the field of polymer membranes for H₂ purification. Although the
7 transport performances of polymeric membranes for H₂ purification are not as attractive, but it is
8 commercially more viable to scale up the fabrication of polymer membranes as compared to the
9 inorganic membranes.
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18 There are two types of polymer membranes classified based on transport mechanisms:
19 solution-diffusion and facilitated transport membranes. The CO₂-selective polymeric solution-
20 diffusion membranes cannot be operated at high temperatures due to low CO₂/H₂ selectivity.
21 However, the facilitated transport membranes appear to exhibit attractive transport performances
22 at high operating temperatures [6-10]. The early facilitated transport membranes, supported
23 liquid membranes and ionic liquids, showed attractive transport performances. But, they
24 suffered from severe transport instabilities because of low resistances to the high pressure
25 difference across the membrane, carrier leakage, solvent evaporation and slow reaction kinetics
26 [4]. Recently, the water swollen polymeric facilitated transport membranes containing mobile
27 and/or fixed-site CO₂-carriers have shown promising results at both the high-pressure and low-
28 pressure conditions.
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46 The schematic representation of the transport mechanism in a facilitated transport membrane
47 is shown in Figure 2. The reactive gas molecules (like CO₂) in the feed gas react reversibly with
48 the carrier molecules in the polymer matrix. The gas-carrier reaction product diffuses from the
49 feed-side to the permeate-side by the virtue of concentration gradient. The reactive gas
50 molecules are released on the permeate side via the reversible reaction, resulting in the
51 regeneration of the carrier molecules in the membrane.
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6 There have been various amines in the form of mobile and fixed-site CO₂-carriers studied by
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8 Ho and co-workers at different pressures. Various amine carriers, namely potassium salt of α -
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10 aminoisobutyric acid (AIBA-K), glycine-Li, and lithium salt of N,N-dimethylglycine as mobile
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12 carriers, along with polyethylenimine (PEI) and commercial polyvinylamine (PVAm) as fixed-
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14 site carriers, were investigated for transport performances. The amine-containing facilitated
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16 transport membranes have demonstrated exceptional performances with CO₂/H₂ selectivity
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18 higher than 200 and CO₂ permeability greater than 3000 Barrers at about 2 bar and 110°C [9].
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20 The performance of these membranes is typically lowered at higher pressures. The CO₂
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22 permeability reduces due to the “carrier saturation” phenomenon, and the CO₂ flux does not
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24 proportionally increase with increasing the feed pressure. On the other hand, more H₂ molecules
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26 would permeate through the membrane at higher pressures via the solution-diffusion mechanism.
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28 Thus, the CO₂/H₂ selectivity of facilitated transport membranes would drop at higher pressures
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30 relative to the selectivity of membranes at lower pressures.
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38 Xing and Ho have studied the synthesis and performance of amine-containing mixed
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40 matrix membranes for CO₂/H₂ separation at high pressures [10]. The amine carriers were
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42 blended with the crosslinked polyvinylalcohol (PVA) which formed the polymer matrix of the
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44 membrane. PVA was used due to its good chemical and thermal stability, hydrophilicity, and
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46 desirable film forming capacity and the higher reactivity of its hydroxyl groups for crosslinking.
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48 AIBA-K and KOH were used as mobile carriers, and polyallylamine (PAA) and aminosilica
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50 (derived from aminosilane via the sol-gel process) were used as fixed-site carriers for high-
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52 pressure applications [10]. Nano-sized fumed silica (about 7 nm) was used as inorganic fillers.
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54 The chemically crosslinked matrix with the presence of fumed silica was expected to increase the
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56 stability of the membrane against the compressive forces. The feed gas with a certified
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composition of 20% CO₂ and 80% H₂ (on dry basis) was used for transport measurements. The transport results for the membranes of different compositions measured at 15 bar feed pressure and 107°C, with a relative humidity of 73% on the feed side, are summarized in Figure 3. Due to of different membrane compositions, the transport results varied as shown in this figure. Moreover, a temperature sensitivity study of the membrane was performed, and 107°C was concluded as the optimized temperature. Additionally, the effects of feed pressure on CO₂ permeability and CO₂/H₂ selectivity were investigated. The results are summarized in Figure 4. The transport performances of such membranes at different feed pressures are significantly relevant to this work due to the presence of high-pressure syngas as the feed gas for CO₂ removal in an IGCC power plant. A cost-effective two-stage membrane process is proposed in this work for syngas purification in an IGCC power plant, and the transport performances (discussed above) will be used to build the model for the membrane stage operated at high pressures.

As mentioned before, the amine-containing facilitated transport membranes have demonstrated attractive transport performances at 1 – 2 bar feed pressures. The transport performances of membranes with AIBA-K as a mobile carrier and PAA as fixed-site carrier were investigated at low pressures (~ 2 bar) and >100°C. The membranes containing AIBA-K and PAA exhibited 250 CO₂/H₂ selectivity and greater than 3000 Barrers of CO₂ permeability [4,9]. The membranes with an average selective layer thickness of 25µm were used for the transport measurements. Later, Zhao and Ho developed a new generation of facilitated transport membranes by exploring the use of sterically hindered polyamines as fixed-site carriers [12,13]. The membranes containing sterically hindered PAA (poly-N-isopropylallylamine) as a fixed-site along with AIBA-K as a mobile carrier demonstrated desirable transport performance and stability. The membranes with 25 µm selective layer thickness exhibited a CO₂ permeability of

greater than 6000 Barrers and an exceptionally higher CO₂/H₂ selectivity of 350. The membranes containing AIBA-K and sterically hindered PAA demonstrated >430 hours of stable transport performance.

The amine-containing CO₂-selective facilitated transport membranes have exhibited attractive transport performances and stability at different pressures. This study has demonstrated the superior transport performances of membranes at low pressures (2 atm feed pressure) with AIBA-K as the mobile carrier and commercial PVAm as the fixed-site carrier. The membranes with a thickness of 15 µm exhibited > 3000 Barrers of CO₂ permeability with a CO₂/H₂ selectivity of > 200. Additionally, a process modeling study was performed by integrating a membrane process to an IGCC power plant for CO₂ capture. A cost-effective, two-stage membrane process (Stage 1 and Stage 2 operated at high pressure and low pressure, respectively) was proposed and analyzed for CO₂ capture from the syngas in an IGCC power plant. In this process modeling study, the experimentally demonstrated transport performances of the CO₂-selective membranes at high pressures (membrane performances investigated by Xing and Ho as discussed before) were used to model the performance of the high pressure membrane stage (> 10 bar). The low-pressure transport results of the CO₂-selective membranes containing AIBA-K and commercial PVAm (discussed in the following section) were used to model the performance of the low-pressure membrane stage.

3. Experimental

3.1. Materials

Poly(vinylalcohol) 217SB (94 wt%, viscosity of 20.5 – 24.5 mPa-s for 4% aqueous solution) with a 87 – 89% hydrolysis degree, was kindly supplied by Kuraray America, Inc., Houston, TX.

Lupamin[®] 9095 (a polyvinylamine (PVAm)-based commercial product) was kindly provided by BASF AG, Germany. The product comprised more than 60% by weight of formate salts and the rest containing PVAm. 2-Aminoisobutyric acid (AIBA) with 99.46% purity was obtained from Chem-Impex International (WoodDale, IL). 3-Aminopropyltriethoxysilane (APTEOS, 99%), glutaraldehyde (GA) (50 wt% aqueous solution), ethylene diamine (EDA) (>99%), and potassium hydroxide (>85%) were purchased from Sigma-Aldrich. Triethylenetetraamine (TETA) (> 60%), which was purchased from Fisher Scientific, contained 40% of cyclic and branched triethylenetetraamines with about 60% of linear TETA.

The nanoporous polysulfone support used in the membrane fabrication was kindly provided by NL Chemical Technology, Inc. in Mount Prospect, IL. The support had a pore size of about 9 nm and a porosity of about 7%.

Specialty feed gas mixtures with a certified composition of 20% CO₂, 40% H₂, 40% N₂, and 50 ppm H₂S were purchased from Praxair, Inc. (Danbury, CT) for the gas permeation measurements. Pre-purified argon was purchased from Praxair, Inc. and used as sweep gas, carrier gas, and reference gas for gas chromatography. Pre-purified helium and oxygen used for the sulfur chemiluminescent detector (SCD) were also obtained from Praxair, Inc.

3.2. Membrane preparation

The first step for lab-scale membrane synthesis was the preparation of partially crosslinked PVA solution. PVA 217SB was dissolved in water in a 250-ml glass conical flask to obtain a solution with the desired 10 – 11% concentration. The aqueous PVA solution was heated to 80°C with continuous stirring for 2 hours. The KOH solution (about 30 – 40% in water) was added dropwise to the PVA solution under gentle stirring. The solution was mixed for 30 minutes after the addition of KOH. Subsequently, the crosslinking reaction was started by

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5 adding glutaraldehyde (GA) solution dropwise under vigorous stirring at 80°C. The reaction was
6 carried out for about 150 minutes after which it was stopped by transferring the reaction flask to
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8 a cold stir plate with continued gentle mixing. The total reaction mixture volume in this case
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10 was about 130 ml. The crosslinking was targeted at the molar degree of 15%. The total solid
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12 content in the crosslinked PVA solution was targeted at 14%, consisting of 11% crosslinked
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14 PVA and 3% KOH.
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20 The carrier solution essentially contained a mixture of AIBA-K and commercial PVAm
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22 solution. AIBA was neutralized in a solution of KOH at room temperature to prepare AIBA-K
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24 solution, and Lupamin[®] was used as received. The carrier solution was prepared by mixing
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26 Lupamin[®] with AIBA-K solution to yield a solution with an appropriate solid concentration.
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28 The casting solution for the membrane synthesis was prepared by adding the carrier solution
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30 dropwise to the calculated amount of the crosslinked PVA solution under stirring in a 50-ml
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32 glass beaker. The total solid concentration in the casting solution was required to be low enough
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34 to avoid instantaneous gelling of the casting solution. The viscosity of the casting solution
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36 increased due to the interaction of polyamines in the carrier solution with the aldehydic groups in
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38 the crosslinked PVA solution. In order to reduce the kinetics of gelling, EDA or TETA (up to
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40 9% of the total solids) was added to the crosslinked PVA solution before the addition of the
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42 carrier solution. The smaller-size molecule EDA or TETA was believed to interact with the
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44 aldehydic groups prior to the addition of the carrier solution. Thus, the kinetics of gelation or the
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46 rate of increase of viscosity of the casting solution was reduced after adding the carrier solution.
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48 The presence of a lesser amount of free aldehydic groups (due to aldehyde and EDA/TETA
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50 interaction) was believed to reduce the overall interaction of aldehyde groups with the
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polyamine. The casting solution was mixed continuously after the addition of the carrier solution for 40 minutes.

The solution was cast on the nanoporous polysulfone support described earlier after attaining desirable viscosity. A casting solution with a high viscosity was desirable to minimize the penetration of the casting solution into the pores of the substrate. The casting solution with 18% total solid content was centrifuged at 8000 rpm for 3 minutes to remove impurities and air bubbles before it was cast on a flat-sheet nanoporous polysulfone support using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The membrane was cured at 120°C in a convection oven for 6 hours for the complete removal of water and the complete crosslinking reaction of PVA with glutaraldehyde.

The thickness of the selective layer was measured by a Mitutoyo electronic indicator (Model 543-252B, Mitutoyo America Corp, Aurora, IL) with an accuracy of $\pm 0.5 \mu\text{m}$. The selective layer thickness was calculated by subtracting the polysulfone support thickness from the total thickness of the composite membrane. The thickness of the selective layer was controlled at around 15 μm .

3.3. Gas permeation set-up and transport measurements

The gas permeation set-up shown in Figure 5 was used to measure the transport performance of the membranes discussed above. The set-up consisted of mass flow controllers, water pumps and humidifiers to simulate the actual gas compositions in syngas. The membrane to be tested was placed between the upper and lower parts of a rectangular gas permeation cell. The feed and sweep gases entered the cell in a countercurrent configuration at the top and bottom sections of the permeation cell, respectively. The retentate and permeate streams were directed

to the gas chromatograph (GC) for composition analysis after the water removal in the knockout vessels. The thermal conductivity detector (TCD) was used for all the gases except H₂S. The sulfur chemiluminescent detector from Antek instruments L.P. (Houston, TX) was used for H₂S analysis. The membrane performances were evaluated by applying the flux equation using the gas compositions obtained from the GC. The membrane surface area of 2.71 cm² was used for the gas permeation measurements.

4. Results and discussion

4.1. Transport measurements

Representative samples from the synthesized membranes were tested for the transport measurements using the gas permeation set-up described above. The feed gas with 20% CO₂, 40% H₂, and 40% N₂ (dry basis) was used for the transport measurements. The feed and sweep gas flow rates were fixed at 60 cc/min and 30 cc/min (on dry basis), respectively, with water flow rates of 0.03 g/min on both sides. The temperature and feed gas pressure for the tests were 106 °C and 2 bar, respectively.

Table 1 shows the total solid compositions of different membranes synthesized and tested. The average selective layer thickness obtained was 15 µm. Figure 6 summarizes the transport performances for the membranes of different compositions listed in Table 1. Due to the different compositions, the performances varied as shown in this figure. As seen from this figure, the membranes have exhibited more than 3000 Barrers of CO₂ permeability and CO₂/H₂ selectivity greater than 200. An important highlight of these CO₂-selective facilitated transport membranes is to consistently obtain a very high CO₂/H₂ selectivity under >100°C operating temperatures.

Current research activities are focusing on using different mobile carriers such as glycine-K and N,N-dimethylglycine-K combined with the use of different fixed carriers such as PEI and high molecular weight polyvinylamine for this particular application.

4.2. Process design for IGCC based CO₂ capture

The main objective of this work is a cost-effective process design of a membrane technology for H₂ purification from syngas in an IGCC plant. A two-stage membrane process has been proposed with Stage 1 and Stage 2 operated at high and low pressures, respectively. Membrane performances obtained by Xing and Ho [11] at high pressures (> 10 bar) have been used to build the process model for the membrane Stage 1 operated at high pressures. The transport performances obtained by the membranes containing AIBA-K and commercial PVAm at 2 bar (as discussed in the Section 4.1) have been applied to model the performance of Stage 2 membrane process operated at low pressures (< 4 bar). Figure 7 shows the process flow diagram of a proposed two-stage membrane process that can be integrated with the IGCC power plant. Preliminary techno-economic assessments have shown that the target of 90% CO₂ capture and >99% H₂ recovery would not be achieved by a single-stage membrane system. A single-stage process would be able to achieve 90% CO₂ removal. However, it would not be viable to obtain >99% H₂ recovery using a single-stage process at high pressures by incorporating the low selectivity (at high pressures, as demonstrated by Xing and Ho [10]). Thus, a two-stage process offers better perspective with a greater fuel (H₂) recovery. Stage 1 would be the membrane-based separation at high pressures and Stage 2 would be the low-pressure membrane stage for enhancing the H₂ recovery. Stage 2 essentially aids in recovering more H₂ due to significantly higher CO₂/H₂ selectivity obtained at low pressures. Moreover, it is desirable to operate Stage 1

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5 at high pressures because the H₂-rich retentate would be recompressed (~ 32 bar) for the power
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11 One of the cases analyzed for the overall cost assessment was with Stage 1 and Stage 2
12 operated at 15 bar and 4 bar, respectively (Figure 7). As shown in Figure 7, syngas after the low-
13 temperature water-gas-shift (WGS) reaction is at high pressures (~ 53 bar) and high temperatures
14 (~ 235°C). The gas needs to be expanded, cooled and passed through the activated, sulfur-
15 impregnated carbon adsorption bed for mercury removal prior to Stage 1 membrane process at
16 15 bar and 107°C [5]. Significant energy is recovered in expanding the gas from 53 bar to 15
17 bar. The pressure on the sweep side for Stage 1 membrane process was considered as 2 bar. As
18 discussed before, Stage 1 itself would not be adequate enough to give the desired >99% H₂
19 recovery at 90% CO₂ removal. Hence, the CO₂-rich permeate from Stage 1 (Stream 3) was
20 recompressed and cooled prior to Stage 2, operated at 4 bar and 107°C. The pressure on the
21 sweep side of Stage 2 membrane was considered as 1 bar. The H₂-rich retentate from Stage 2
22 (Stream 4) would combine with the retentate from Stage 1 (Stream 2) after recompression. The
23 coupled stream was compressed and heated to 31.7 bar and 196°C, respectively, prior to the gas
24 turbine for large-scale power generation. The CO₂-rich permeate from Stage 2 (Stream 5)
25 undergoes a series of compression and cooling cycle prior to the Selexol[®] unit for H₂S removal
26 at 53 bar and 35°C [5]. The H₂S-rich stream from the Selexol[®] unit (Stream 6) was sent to the
27 Claus unit for sulfur recovery, and the CO₂-rich stream from Selexol[®] (Stream 7) was
28 compressed and sent for sequestration purposes. A Stage 1 feed pressure of 15 bar and Stage 2
29 feed pressure of 4 bar were considered for this case as the transport performances of the amine-
30 containing facilitated transport membranes had been experimentally obtained at similar
31 conditions (discussed in the previous sections). The membrane with a CO₂ permeability of 1296
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5 Barrers and a CO₂/H₂ selectivity of 87 was used for the Stage 1 operated at 15 bar and 107°C
6 (Figure 3). On the other hand, the membrane with a CO₂ permeability of 3500 Barrers and a
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8 CO₂/H₂ selectivity of 200 (as obtained from membranes discussed in Section 4.1 and shown in
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10 Figure 6) was applied to model the performance of Stage 2 operated at 4 bar and 107°C. A
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12 significantly higher CO₂/H₂ selectivity obtained at the low pressure has aided in enhancing the
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14 overall fuel (H₂) recovery via the Stage 2 membrane process. The modeling results for the case
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16 discussed above are shown in Table 2.
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24 The overall techno-economic analysis for an increase in the cost of electricity (COE) was
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26 carried out by taking the GEE IGCC based 550 MW power plant without carbon capture (Case 1
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28 [5]) as the base case. The membrane areas required for the two-stage process were calculated
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30 using the software COMSOL Multiphysics 3.4 (discussed in Section 4.3.1).
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35 The overall cost is typically sensitive to the energy consumption in the proposed carbon
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37 capture process. For the case in discussion (Table 2), the distribution of the energy consumed by
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39 different equipment in the proposed two-stage membrane process for CO₂ removal is shown in
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41 Table 3. As shown in this table, considerable energy was consumed by the recompression steps.
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43 A significant amount of energy penalty arises in the form of the CO₂-rich permeate
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45 recompression and the H₂-rich retentate recompression. Hence, the development of high-
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47 pressure membranes (> 15 bar operating pressure) with improved CO₂/H₂ selectivity would
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49 significantly reduce the recompression energy penalty. The higher the Stage 1 feed pressure, the
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51 lower would be the energy consumed to compress the H₂-rich retentate to 31.7 bar prior to the
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53 gas turbine. The process parameters mentioned in Table 3 reflect the potential impact of the
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55 operating conditions on the overall economics. Later in this study, a cost-sensitivity study is
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57 shown by varying the operating Stage 1 and Stage 2 feed pressures. Stage 1 feed pressure is
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varied from 11 bar to 29 bar, and the Stage 2 feed pressure is changed from 2.5 bar to 4 bar. The cost-sensitivity study would highlight the importance of high-pressure operation for an optimized operating condition for the cost-effective process.

4.3. Process modeling and economics

4.3.1 Membrane process modeling and simulation

The simulation of the gas transport through the membrane module was performed using a one-dimensional model. Molar balances can be written for each component as shown in Equations 1, 2, and 3.

$$\frac{dn_{fi}}{dz} = -\pi d J_i \quad (1)$$

$$\frac{dn_{si}}{dz} = -\pi d J_i \quad (2)$$

$$J_i = P_i(p_f \times x_i - p_s \times y_i) \quad (3)$$

In the Equations 1 and 2, the left hand sides represent the change in the molar flow rate of the component with respect to position in the feed and sweep sides, respectively. The right hand sides represent the permeation of the components through the membrane. As seen from Equation 3, the flux of component through the membrane is defined as the product of permeance (P_i) and the partial pressure difference. Due to the absence of a sweep stream for both Stage 1 and Stage 2 in the membrane process, the temperatures of the feed gas streams are unlikely to change along the length of the membrane module. Thus, Stage 1 and Stage 2 are assumed to operate isothermally.

The boundary conditions are set by the known molar flow rates at the feed and sweep inlets.

They are listed as follows:

For the Stage 1 membrane process:

At $z = 0$:

$$n_{fCO_2} = x_{CO_2} \times n_{to}, \quad n_{fH_2} = x_{H_2} \times n_{to}, \quad n_{fH_2O} = x_{H_2O} \times n_{to}, \quad \text{and} \quad n_{fH_2S} = x_{H_2S} \times n_{to}$$

At $z = L$:

$$n_{sCO_2} = 0, \quad n_{sH_2} = 0, \quad n_{fH_2O} = 0, \quad \text{and} \quad n_{fH_2S} = 0 \quad (\text{No sweep inlet gas})$$

where n_{to} is the molar flow rate of the feed stream (Stream 1 in Figure 7) entering the Stage 1 membrane process.

For the Stage 2 membrane process:

At $z = 0$:

$$n_{fCO_2} = x_{CO_2} \times n_{to}, \quad n_{fH_2} = x_{H_2} \times n_{to}, \quad n_{fH_2O} = x_{H_2O} \times n_{to}, \quad \text{and} \quad n_{fH_2S} = x_{H_2S} \times n_{to}$$

At $z = L$:

$$n_{sCO_2} = 0, \quad n_{sH_2} = 0, \quad n_{fH_2O} = 0, \quad \text{and} \quad n_{fH_2S} = 0 \quad (\text{No sweep inlet gas})$$

For this stage; n_{to} , x_{CO_2} , x_{H_2} , x_{H_2O} and x_{H_2S} correspond to Stream 3 in Figure 7. The permeate outlet from Stage 1 is the feed inlet to Stage 2 (Figure 7).

This system of equations was solved using the Partial Differential Equation (PDE) mode of COMSOL Multiphysics 3.4 which uses the finite element method to solve them.

The important assumptions of the membrane process model are as follows:

1. The module operates at steady state in a countercurrent configuration.
2. The pressure drops are negligible.
3. There is no axial mixing on both the lumen and shell sides.
4. The gas permeances remain constant along the module length.

5. The $\text{H}_2\text{O}/\text{CO}_2$ selectivity is assumed as 3 (similar to $\text{H}_2\text{S}/\text{CO}_2$ selectivity) for both Stage 1 and Stage 2 in the membrane process.

This model was used to evaluate the membrane areas required for the Stage 1 and Stage 2 in the membrane process, for a given degree of CO_2 removal and H_2 recovery for both stages. The results for 90% CO_2 capture and > 99% H_2 recovery using the two-stage membrane process for one of the cases is shown in Table 2.

4.3.2 Process Economics

The overall process modeling was targeted at 90% CO_2 capture, 99% H_2 recovery and close to 50 ppm of H_2S in the purified syngas stream. The financial model used to calculate the economic parameters for the process is shown in Table 4. The economic methodology shown in Table 4 was obtained and adapted from previous studies [14-18]. The fixed parameters used in the process modeling are listed in Table 5.

The membrane replacement cost (*MRC*) of $\$2/\text{ft}^2$ (as shown in Table 4) was based on the current membrane price for the gas separation and water desalination applications [14]. The cost of the membrane housing for Stage 1 membrane module would be more expensive than the cost for Stage 2 membrane module due to high operating pressure in Stage 1. Hence, a higher membrane housing and element cost (*MC*) was used for Stage 1 ($\$5.34/\text{ft}^2$) relative to Stage 2 ($\$2.50/\text{ft}^2$). The cost for the high pressure housing was adapted from the cost reported for the natural gas-based applications at high pressures [14,15].

The final CO_2 compression and drying was considered by using the combination of compressor and pump to reduce the overall energy consumption. The critical pressure of CO_2 is about 74.8 bar at 30°C . The CO_2 -rich stream could be compressed to 74.8 bar and subsequently pumped from 74.8 bar to 150 bar. A multiple staged compressors with inter-stage cooling were

considered to reduce the overall energy consumption [19-22]. The purchase costs of \$594/kW for the compressor-related equipment and \$846/kW for the expander-related equipment were obtained from the baseline document of the U.S. Department of Energy [5]. The equipment cost index for pumps and compressors was taken from [20].

The expansion and compression processes were assumed to be polytropic in nature. The polytropic efficiency was considered to be 85% as reported in previous studies [23-26]. The energy consumption of each stage in the CO₂ compressor was evaluated using the following equation given by Mohitpour [25], which takes into account the compressibility of CO₂.

$$E_c = \frac{Z_{ave} \times Q_c \times \frac{\gamma RT}{\gamma - 1} \times \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]}{\eta_c \times 1000} \quad (4)$$

where E_c is the energy consumption of the compressor, Z_{ave} is the average compressibility of CO₂, Q_c is the molar flow rate of the gas through the device, γ is the polytropic index, R is the universal gas constant, T is the inlet absolute temperature of the gas, P_1 is the inlet pressure, P_2 is the outlet pressure, and η_c is the efficiency of compression (polytropic efficiency $\times$ mechanical efficiency). An online source was used to determine the compressibility factor and other physical properties of the gases [26].

The energy consumption of the pump (for liquids) was estimated using the expression given by Vogelesang [27].

$$E_p = \frac{Q_p \times \Delta p}{\eta_p \times 36} \quad (5)$$

where Q_p is the liquid volumetric flow rate to the pump, Δp is the pump head, and η_p is the pump efficiency which was taken as 85%. The pump purchase cost was evaluated using the Equation 6 [14]:

$$\text{Pump Cost in \$ million} = \frac{1.11 \times E_p}{1000} + 0.07 \quad (6)$$

where E_p is the energy consumption of the pump.

4.4. Cost sensitivity

Table 6 summarizes the modeling results after applying the economic model discussed above. An increase in the COE for incorporating a two-stage membrane process in discussion was estimated to be 17.6% for Stage 1 and Stage 2 operated at 15 bar and 4 bar, respectively. The transport performances obtained by Xing and Ho [10] for high pressures and some recent low-pressure transport performances (discussed in Section 4.1) were used for evaluating the membrane areas. The estimate of 17.6% increase in COE is a highly attractive estimate obtained from applying the experimentally demonstrated membrane transport performances.

The energy consumption distribution (shown in Table 3) highlighted a significant energy penalty due to the compression power. Therefore, the cost sensitivity studies based on different feed pressures and membrane transport parameters are discussed in the following sub-sections. Figure 8 shows a schematic representation of the analytical procedure used for cost-sensitivity estimation. A detailed explanation of the steps involved in the estimation is summarized in Appendix B.

4.4.1. Stage 1 feed pressure

Xing and Ho investigated the transport performances at different pressures from 5 bar to 15 bar [10]. As discussed before, Figure 4 shows the sensitivity of the CO₂ permeability and CO₂/H₂ selectivity with the feed gas pressure. This set of data was used to extrapolate and predict the membrane performance at pressures higher than 15 bar. Along with this set of data, the extrapolated data were used to evaluate the overall increase in the COE with different Stage 1 feed pressures (Figure 9).

As seen from Figure 9, the increase in the COE initially shows a dropping trend on increasing Stage 1 feed pressure from 11 bar. A higher Stage 1 feed pressure would reduce the energy consumption for the H₂-rich retentate recompression. The increase in the COE reaches an optimum of 15.5% at 23 bar pressure, and the trend initiates to increase for a Stage 1 pressure of greater than 23 bar. The CO₂ permeability essentially drops at higher pressures (carrier saturation). Thus, the increase in the capital cost corresponding to the larger membrane areas required (by virtue of reduction in permeability) would overpower the cost reduction due to the lower energy penalty at the higher pressure operation. Hence, an increasing trend is observed for >23 bar Stage 1 feed pressure. However, a 15.5% increase in the COE is a significantly attractive estimate compared to the ~ 39% increase in the COE evaluated for the well-known Selexol[®] process.

4.4.2. Stage 2 feed pressure

A trend similar to Stage 1 feed pressure can be observed for the sensitivity of the COE with Stage 2 feed pressure. As shown in Figure 10, the optimum pressure for Stage 2 corresponds to 3 bar. An increase in Stage 2 pressure would increase the energy consumption for Stage 1 permeate recompression. However, it would also reduce the membrane area

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5 requirement for Stage 2 due to the larger CO₂ driving force. Thus, a Stage 2 pressure of 3 bar
6 pressure appears to be an optimum pressure of operation at 107°C.
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11 Stage 1 and Stage 2 feed pressures of 23 bar and 3 bar, respectively, at 107°C were
12 determined as an optimized operating condition. Hence, all the following sensitivity studies are
13 evaluated at these optimized feed pressures.
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19 4.4.3. Stage 1 CO₂/H₂ selectivity

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22 Figure 11 shows the sensitivity of the COE with the change in Stage 1 membrane CO₂/H₂
23 selectivity. The plot shows that developing a membrane with a higher selectivity at the Stage 1
24 optimum operating pressure of 23 bar would reduce the overall cost due to the reduction in the
25 membrane area for Stage 2. The larger quantity of fuel (H₂) would be recovered in Stage 1 by
26 virtue of the higher CO₂/H₂ selectivity. Thus, the lesser membrane area would be required for
27 Stage 2 to enhance the overall H₂ recovery.
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37 4.4.4. Stage 2 CO₂/H₂ selectivity

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40 The sensitivity of COE to Stage 2 CO₂/H₂ selectivity is shown in Figure 12. Contrary to
41 Stage 1 CO₂/H₂ selectivity, the COE tends to increase with an increase in the CO₂/H₂ selectivity
42 of Stage 2 membrane. This can be attributed to the reduction in the CO₂ driving force by virtue
43 of more CO₂ selectively permeating through Stage 2. Thus, a larger membrane area would be
44 required for a given degree of separation in Stage 2.
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54 4.4.5. Membrane thickness

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57 All the cases discussed above were evaluated by considering 5 µm as the thickness of the
58 selective layer. The gas permeance (permeability per unit thickness) would typically increase on
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reducing the membrane thickness. An increase in the CO₂ permeance would essentially reduce the membrane area required for a given degree of separation. The reduction in the membrane area would translate into a reduction in the capital cost. Figures 13 and 14 show the change in the COE with membrane thickness for Stage 1 and Stage 2, respectively. The overall increase in COE reduces on increasing the permeance by virtue of reduction in the thickness of the selective layer for both Stage1 and Stage 2. However, the overall cost appears to be more sensitive to the Stage 1 membrane thickness as compared to the Stage 2 membrane thickness. This is because the capital cost per unit area for Stage 1 membrane module is significantly higher than that for Stage 2 membrane module.

5. Conclusions

This study has shown a cost-effective membrane-based process design for CO₂ capture in an IGCC power plant. Amine-containing CO₂-selective facilitated transport membranes were synthesized and tested for transport performances. The transport performances of amine-containing membranes at different pressures were applied to the techno-economic model for CO₂ removal in an IGCC power plant. The final conclusions from this work can be summarized as follows:

- 1.) The increase in the COE was calculated based on the transport performances of the membranes synthesized by Ho and co-workers. An increase in the COE of 17.6% was estimated by using the experimentally demonstrated membrane transport performances. A cost-sensitivity study showed an increase in the COE in the range of 14 – 18% at different conditions, using the two-stage process for CO₂ removal from the syngas in an IGCC power plant.

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6 2.) This study has indicated the need for the development of membranes that could operate at
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8 high pressures (greater than 15 bar) with desirable transport performances. A high-pressure
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10 operation could significantly reduce energy consumption.
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13 3.) In this study, an experimentally demonstrated H₂S/CO₂ selectivity of 3 was considered. The
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15 solvent based Selexol[®] process was used for H₂S separation in the process modeling and a
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17 5% increase in the COE was included for the Selexol[®] process [18]. However, the H₂S/CO₂
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19 selectivity could be improved further to develop a membrane-based process for H₂S
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21 separation. The overall cost could be potentially be reduced significantly by replacing the
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23 Selexol[®] process with the membrane process of improved H₂S/CO₂ selectivity, resulting in
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25 an overall cost-effective three-stage process for CO₂ and H₂S removal.
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59 **Appendix A**

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The % COE increase and capture cost are defined as follows [4,13]:

$$\bullet \quad \% \text{ COE increase} = \frac{\text{COE}_{\text{capture}} - \text{COE}_{\text{no capture}}}{\text{COE}_{\text{no capture}}} \times 100$$

The COE is based on the net power output of the plant. In this study, the net power output (550 MW) has been kept the same for both the base plant and the plant with carbon capture, which is consistent with other detailed cost studies [14,18]. For the same net power output, the power plant with capture is larger in terms of total power output than the one without capture by virtue of the parasitic energy consumption. This also means that the untreated flue gas flow rate and consequently the CO₂ flow rate are higher for the plant with capture due to the additional fuel burnt to make-up the extra power.

Appendix B

The steps involved in the overall cost estimation shown in Figure 8 are described as follows:

1. Based on the pressure of Stream 1, the amount of energy recovered in the gas expansion process via the turbo-expander is evaluated. This determines the pressure, flow rate and composition of Stream 1.
2. Using the above information and the transport parameters of the membrane (permeance and selectivity), a set of flux-based differential equations are solved to obtain the membrane area required for Stage 1 aimed at >90% CO₂ removal. This determines the flow rates of Stream 2 and Stream 3.
3. The overall mass balance aids in determining the CO₂ removal and H₂ recovery targets for Stage 2. The Stage 2 membrane simulation is carried out using the membrane parameters (permeance and selectivity) to evaluate the membrane area required for an overall 90% CO₂ removal in Stream 5 and >99% hydrogen recovery (based on Stream 2 and Stream 4).

4. Using the above membrane areas, pressures and flow rates and the total power consumption (Stream 2, Stream 3, Stream 4, Stream 5 and Stream 7 recompression), the % increase in the COE can be calculated using the procedure highlighted in Table 4.

Nomenclature

d diameter of the hollow fiber, cm

E_c compressor power consumption, kW

E_p pump power consumption, kW

J steady-state flux, mole/(m²·s)

n molar flow rate, mole/s

P_1 inlet pressure to the compressor, bar

P_2 outlet or downstream pressure, bar

p pressure, bar

Δp the design head of the pump, bar

Q_c gas molar flow rate to the compressor, mole/s

Q_p liquid volumetric flow rate, m³/hr

R universal gas constant, 8.314 J/mol/K

T absolute temperature, K

x mole fraction on the feed side

y mole fraction on the permeate or sweep side

z position variable along the length of the hollow fiber, cm

Z_{ave} average compressibility of the gas between the inlet and outlet conditions of the compressor

Greek letters

γ polytropic index

η_c efficiency of compression

η_p efficiency of pump

Subscripts

f feed side

i, j species

s sweep side

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Tables

Table 1. The total solid compositions of different membranes containing AIBA-K and commercial PVAm synthesized with an average 15 μm thickness of the selective layer.

Parameter/Membrane	M-1	M-2	M-3	M-4	M-5	M-6
Crosslinked PVA (%)	33	33	29	34	28	30
KOH (%)	13	13	14	13	18	17
AIBA-K (%)	22	20	26	27	22	23
Lupamin [®] (%)	22	24	23	17	21	21
TETA (%)	7	7	6	7	0	0
EDA (%)	0	0	0	0	8	7
APTEOS (%)	3	3	2	2	3	2

Table 2. The modeling results for the two-stage membrane process for syngas purification in an IGCC power plant with the Stage 1 membrane process operated at 15 bar and Stage 2 membrane process operated at 4 bar.

Parameter	Value
Net plant capacity (MW)	550
Stage 1 feed pressure (bar)	15
CO ₂ permeability for Stage 1 (Barrer)	1296
CO ₂ /H ₂ selectivity for Stage 1	87
Stage 1 membrane area (million ft ²)	3.52
Stage 2 feed pressure (bar)	4
CO ₂ permeability for Stage 2 (Barrer)	3500
CO ₂ /H ₂ selectivity for Stage 2	200
Stage 2 membrane area (million ft ²)	2.17
Overall CO ₂ capture (%)	90
Overall H ₂ recovery (%)	99.3
Total compression power (MW)	24.16

Table 3. The distribution of the energy consumed (%) by different equipment in the proposed two-stage membrane process for CO₂ removal from syngas in an IGCC power plant.

Equipment	Percentage contribution in energy consumption
Retentate recompression	22.55
CO ₂ recompression	64.60
CO ₂ pump	2.65
Stage 1 permeate recompression	10.20

Table 4. The economic model and methodology used to evaluate the economic parameters for the proposed two-stage membrane process for CO₂ removal from syngas in an IGCC power plant. The economic methodology was obtained and adapted from previous studies [14-18].

<i>Total plant investment (TPI)*</i>	
Total membrane module cost (MC):	\$5.34/ft ² (includes the membrane housing) for >11 bar pressure \$2.50/ft ² (includes the membrane housing) for ≤3.5 bar pressure
Installed compressor and pump cost (CC):	CC (described below)
Installed blower cost (BC):	BC (described below)
Installed expander cost (EC):	EC (described below)
Installed heat exchanger cost (HC):	HC (described below)
Fixed cost (FC):	MC+CC+BC+EC+HC
Base plant cost (BPC):	1.12×FC
Project contingency (PC):	0.20×BPC
Total facilities investment (TFI):	BPC+PC
Start-up cost (SC):	0.10×VOM
<i>TPI*</i>	<i>TFI+SC</i>
<i>Annual variable operating and maintenance cost (VOM)</i>	
Contract and material maintenance cost (CMC):	0.05×TFI
Local taxes and insurance (LTI):	0.015×TFI
Direct labor cost (DL) (based on 8 h/day per 25 MMSCFD or 366 mole/s of feed):	\$15/hr
Labor overhead cost (LOC):	1.15×DL
Membrane element or replacement cost (MRC):	\$2/ft ² of membrane
Make-up power cost (MuPC):	\$0.077/kWh
<i>VOM*</i>	<i>CMC+LTI+DL+LOC+MRC+WC+MuPC</i>
<i>Annual capital related cost (CRC)</i>	<i>0.125×TPI</i>
<i>Annualized Cost (AC)</i>	<i>VOM+CRC</i>
<i>Other assumptions</i>	
Membrane life:	4 years
On-stream factor (OSF):	85%
Base cost of electricity (original power plant without capture) (COE)*:	\$0.086/kWh-net

*All the cost estimated are in 2007 U.S. dollars.

Table 5. Fixed parameters used in the process modeling for incorporating the two-stage membrane process for CO₂ removal from syngas in an IGCC power plant.

Feed gas composition from low temperature WGS reactor	31% CO ₂ , 44% H ₂ , 23% H ₂ O
CO ₂ capture	90%
H ₂ recovery	>99%
H ₂ S in the H ₂ enriched stream	50 ppm
H ₂ S removal	Selexol
Net plant output	550 MW

Table 6. Summary of the process modeling results for the first case evaluated by incorporating the transport performances of amine-containing membranes obtained by Ho and co-workers [11-13] into the process model.

Stage 1 feed pressure (bar)	15
Stage 2 feed pressure (bar)	4
Stage 1 temperature (°C)	107
Stage 2 temperature (°C)	107
CO ₂ permeability for membrane Stage 1 (Barrers)	1296
CO ₂ /H ₂ selectivity for membrane Stage 1	87
Stage 1 membrane area (million ft ²)	3.52
CO ₂ permeability for membrane Stage 1 (Barrers)	3500
CO ₂ /H ₂ selectivity for membrane Stage 1	200
Stage 2 membrane area (million ft ²)	2.17
Net plant capacity (MW)	550
Energy consumption for CO ₂ capture (MW)	30
Cost of electricity for the base plant without capture (COE)*	\$0.086/kWh
Estimated % increase in the COE*	17.6

*All the economic estimates are in 2007 U.S. dollars.

Figure captions

Fig. 1. Schematic representation of the IGCC power plant with carbon capture

Fig. 2. Schematic of gas permeation through a facilitated transport membrane (reproduced from [12,13]).

Fig. 3. Plot of CO₂/H₂ selectivity vs. CO₂ permeability for amine-containing mixed matrix membranes of different compositions measured at 15 bar feed pressure at 107°C, using 20% CO₂ and 80% H₂ (dry basis) as the feed gas with 73% relative humidity (the results have been plotted using the transport data published in [10]).

Fig. 4. Plot of CO₂ permeability and CO₂/H₂ selectivity with different feed pressures of amine-containing mixed matrix membranes measured at 107°C using 20% CO₂ and 80% H₂ (dry basis) as the feed gas (the results have been plotted using the transport data published in [10]).

Fig. 5. Schematic of the gas permeation apparatus for gas transport measurements (reproduced from [12,13]).

Fig. 6. Plot of CO₂/H₂ selectivity vs. CO₂ permeability for membranes of different compositions containing AIBA-K and commercial PVAm tested at 2 bar and 106°C using 20% CO₂, 40% H₂, and 40% N₂ (dry basis) as the feed gas and argon as the sweep gas. The dry feed and sweep gas flow rates used were 60 cc/min and 30 cc/min, respectively, with 0.03cc/min of water flow rates on both sides.

Fig. 7. Process flow diagram for the two-stage membrane process for CO₂ removal from syngas in an IGCC power plant.

Fig. 8. Schematic representation of the cost calculation procedure.

Fig. 9. Plot of the increase in the cost of electricity (COE) with different Stage 1 feed pressures at 107°C and 3 bar Stage 2 feed pressure.

Fig. 10. Plot of the increase in the cost of electricity with different Stage 2 feed pressures at 107°C and 15 bar Stage 1 feed pressure.

Fig. 11. Plot of the increase in the cost of electricity with different Stage 1 CO₂/H₂ selectivities at 107°C, 23 bar Stage 1 feed pressure, and 3 bar Stage 2 feed pressure.

Fig. 12. Plot of the increase in the cost of electricity with different Stage 2 CO₂/H₂ selectivities at 107°C, 23 bar Stage 1 feed pressure, and 3 bar Stage 2 feed pressure.

Fig. 13. Plot of the increase in the cost of electricity with different Stage 1 membrane thicknesses at 107°C, 23 bar Stage 1 feed pressure, and 3 bar Stage 2 feed pressure.

Fig. 14. Plot of the increase in the cost of electricity with different Stage 2 membrane thicknesses at 107°C, 23 bar Stage 1 feed pressure, and 3 bar Stage 2 feed pressure.

Figures

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