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CO₂-selective membranes for hydrogen production and CO₂ capture - Part II: Techno-economic analysis

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ABSTRACT

Syngas processing often requires separation of CO₂ and hydrogen for hydrogen production, and the resulting CO₂-enriched stream presents an opportunity for simultaneous CO₂ capture. For example, syngas-based integrated gasification combined cycle (IGCC) power plants are envisioned as an efficient means of producing power from coal where CO₂ capture technologies can be applied relatively easily. Membrane technology is an attractive approach for CO₂ capture because of inherent process advantages such as simplicity, reliability, compactness and modularity. This paper (Part II of a two-part study) performs techno-economic analysis for CO₂-selective membranes in three hydrogen production or utilization applications: methane reformer/pressure swing adsorption processes, oxygen-blown coal-fired IGCC power plants using GE gasification technology, and air-blown coal-fired IGCC power plants using Transport Integrated Gasification (TRIG) technology. These processes require membranes with CO₂/H₂ selectivities of 10-20, which can be provided using PolarisTM membranes. Hybrid approaches using a combination of membrane and cryogenic processes are evaluated for the production of high-pressure liquid CO₂ ready for utilization or sequestration. The optimal membrane CO₂/H₂ selectivity and influence of CO₂ capture rate on the cost of CO₂ capture are determined, providing general guidelines for future membrane development. The cost of CO₂ capture with these membrane processes depends not only on the feed CO₂ partial pressure, but on the feed CO₂ concentration as well.

Keywords:

CO₂-selective membrane, hydrogen purification, CO₂ capture, syngas, process designs

Nomenclature

\$MM	million US dollar
A_m	membrane area (cm ²)
gpu	gas permeation unit [10 ⁻⁶ cm ³ (STP)/(cm ² s cmHg)]
IGCC	integrated gasification combined cycle
l	film thickness (cm)
MMscfd	million standard cubic feet per day
N_P	total steady state flux across the membrane [cm ³ (STP)/s]
p_1	downstream pressure (bar)
p_2	upstream pressure (bar)
P_A	permeability of a polymer to gas A (Barrer)
P_A/l	permeance of a composite membrane to gas A (gpu)
TRIG	Transport Integrated Gasification Technology
$x_{1,A}$	mole fraction of component A in the permeate
$\bar{x}_{2,A}$	average concentration of component A in the membrane upstream
$x_{F,A}$	mole fraction of component A in the feed entering the module
$x_{R,A}$	mole fraction of component A in the residue exiting the module

Subscript

1	membrane downstream side
2	membrane upstream side
A	component A

1. Introduction

Syngas refinery and petrochemical operations often require separation of CO₂ and hydrogen for various reasons, including hydrogen production, syngas ratio adjustment for chemicals production, and, in the future, CO₂ capture to mitigate emissions to the atmosphere that are responsible for global climate change. Currently, when required, CO₂ is removed from syngas using adsorption or absorption technologies [1]. Membranes are an attractive process alternative for gas separation, due to the following intrinsic advantages [2-4].

- (1) Simple and passive. Membrane separations provide a one-pass operation without moving parts, except in the associated auxiliary equipment. Membrane systems can be operated in remote areas with minimal maintenance.
- (2) Compact and light. Membrane systems often have small footprints and good weight efficiency.
- (3) Modular and scalable. As demand changes, membrane systems have the flexibility to be scaled up or down gradually and easily.

Many prior studies have examined membrane technology for H₂ purification and/or CO₂ capture from syngas streams. Both CO₂-selective and H₂-selective membranes have been considered [4-6]. CO₂-selective membranes are often based on rubbery polar polymers and are preferred for processes that operate at ambient or sub-ambient temperatures [7-24]. In contrast, H₂-selective membranes are typically based on rigid glassy polymers [25-28] or ceramic and metallic materials [29-31] that are preferred for operations at elevated temperatures. These different types of membrane materials have been proposed for use in a variety of syngas applications requiring CO₂ separation including H₂ production plants [32-34] and IGCC power plants [35-38]. In the cases where techno-economic evaluations of the membrane processes were

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4 conducted, they are often based on a CO₂ capture rate of 90%, which is the current target rate set
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6 by the U.S. Department of Energy (DOE) for new CO₂ capture technologies being considered for
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8 use at power plants [5,18,39,40]. There are few systematic studies that examine the cost of CO₂
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10 capture for membrane systems as a function of the CO₂ capture rate and compare these costs
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12 between different syngas applications. The impact of capture rate on cost is particularly relevant
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14 with the growing need for CO₂ in enhanced oil recovery (EOR) operations.
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18 This study examines the CO₂-selective Polaris™ membrane for use in H₂ purification and
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20 CO₂ capture from syngas. Part I of this study described the following three-stage evaluation of
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22 the membranes as suitable materials for this application [4]:
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26 (1) laboratory testing of small membrane stamps (30 cm² membrane area),
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28 (2) field testing of bench-scale membrane modules (1 – 4 m² membrane area) in a pilot-scale
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30 skid at a syngas production plant, and
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32 (3) a full membrane system demonstration processing 500 lb/hr of coal-derived syngas and
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34 producing liquid CO₂ ready for sequestration [4].
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38 In Part I, the membranes were shown to exhibit mixed-gas CO₂/H₂ selectivities of 10 – 20,
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40 depending on temperature and feed pressure [4].
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43 Part II of this study evaluates CO₂-selective membrane processes for hydrogen purification
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45 and CO₂ capture in three types of H₂ production/utilization processes: a methane
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47 reformer/pressure swing adsorption process, oxygen-blown coal-fired IGCC power production
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49 using GE gasifier technology, and air-blown coal-fired IGCC power production using TRIG
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51 gasifier technology. The conditions of these syngas streams have been reported in the literature
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53 and will be used in this study. The impact of CO₂/H₂ separation properties and the targeted CO₂
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capture rate on the capital and operating expenses for each commercial separation are investigated.

2. Background on membrane process simulations and cost analysis

2.1. Membrane process simulations

The process design calculations for this study were performed using a commercial process simulator, ChemCAD 6.3 (ChemStations Inc., Houston, TX), enhanced with a non-isothermal membrane modeling code. The membrane simulation is based on finite element analysis, and a thermodynamic package that uses the Soave-Redlich-Kwong equation of state is used. Similar methods for simulating continuous membrane separations have been described elsewhere [41-44].

If the stage-cut of a membrane unit (defined as the percentage of the feed gas entering the permeate) is low (< 20%), the following equation can provide a rough estimate of the membrane separation performance in the crossflow mode [36,45,46]:

$$\frac{P_A}{l} = \frac{N_P x_{1,A}}{A_m \cdot (p_2 \bar{x}_{2,A} - p_1 x_{1,A})} \quad (1)$$

where P_A/l is the permeance of gas A, N_P is the total permeate flow rate, $x_{1,A}$ is the mole fraction of component A in the permeate and $\bar{x}_{2,A}$ is the average concentration of component A in the membrane upstream. The parameter of $\bar{x}_{2,A}$ is estimated as the logarithmic mean of component A concentration on the membrane upstream face:

$$\bar{x}_{2,A} = \frac{x_{F,A} - x_{R,A}}{\ln(x_{F,A}/x_{R,A})} \quad (2)$$

where $x_{F,A}$ and $x_{R,A}$ are the mole fraction of component A in the feed gas entering the module and the residue gas exiting the module, respectively.

2.2. Cost assumptions used in the analysis

The economics of membrane systems are determined by many factors including the membrane separation properties, feed gas stream conditions, and the product requirements [35,46-50]. To evaluate the relative attractiveness of using membrane systems for syngas treatment, the cost of CO₂ capture using a membrane unit can be estimated and compared side-by-side with other separation technologies.

Table 1 summarizes the cost assumptions used in this study. The membrane skid has an estimated installed cost of \$500/m² membrane area, which includes membrane modules, module housings, valves, instrumentation, piping and frame structures [35,51]. This cost is typical for current custom-built membrane systems containing spiral-wound membrane modules for CO₂ removal from natural gas, a process involving high-pressure flammable gases similar to those present in CO₂ removal from syngas [35]. The other assumptions are taken from a 2013 U.S. DOE report [39] on CO₂ capture from IGCC syngas where an absorption technology (Selexol) is used as a baseline for estimating pre-combustion CO₂ capture cost.

Table 1

Cost assumptions used in this study for the economic analysis of membrane processes [35,39].

Category	System parameter	Value
Capital expenses	Membrane skid	\$500/m ²
	Compressor and refrigeration skid	\$1000/kW
	Installation cost multiplier:	
	Membrane skid	1.85
	Compressor and refrigeration skid	1.61
	Project contingencies	20%
Operating expenses	Process contingencies	20%
	Capital depreciation and financing	15%/year
	Annual membrane replacement cost	\$100/m ²
	Electricity cost	\$0.06/kW

3. Membranes for CO₂ capture in hydrogen production plants

3.1. Background on hydrogen production

Most hydrogen is currently produced by steam reforming of light hydrocarbons such as methane [52,53]. A block flow diagram of a conventional steam reformer-pressure swing adsorption (PSA) H₂ plant is shown in Fig. 1. The feed stream (typically CH₄) is first pretreated to remove trace amounts of sulfur that would poison later-stage catalysts. The gas is then heated to 500 °C, mixed with excess steam, and passed through externally fired reformer tubes filled with nickel catalyst. Methane is converted to carbon monoxide (CO), CO₂, and H₂ according to the reactions:

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Parameter	① PSA feed	② H ₂ product	③ PSA tail gas
Composition (vol%)			
H ₂	78.0	99.9	36.1
CH ₄	1.0	0.1	3.0
CO	2.0	—	6.1
CO ₂	19.0	—	54.8
Flow Rate (MMscfd)	100	67.2	32.8
Pressure (bar)	30	30	5

Fig. 1. Block flow diagram of a steam methane reformer-pressure swing adsorption (PSA) H₂ plant.

Steam reforming is an equilibrium reaction. The typical gas mixture leaving the reformer contains about 76% H₂, 10% CO₂, 12% CO, and 1-2% unreacted CH₄ [52,53]. All composition data for this paper are expressed as vol%. The gas is cooled and fed to a CO shift converter, where most of the CO is converted to CO₂ while producing additional H₂ by the reaction:

This reaction does not go to completion; typical shift converter exit streams contain about 78% H₂, 1% CH₄, 2% CO, and 19% CO₂. The exit gas is cooled to about 30°C and fed to a pressure swing adsorption (PSA) separator. The PSA unit produces an essentially pure H₂ overhead stream and a low-pressure tail gas containing CO, CH₄, CO₂, and H₂. This PSA tail gas stream contains 15% of the H₂ produced by the process, and is used as fuel to heat the reformer.

Hydrogen has much higher value as a chemical than as fuel, and therefore, many H₂ recovery processes from the PSA tail gas, including ones based on membranes, have been evaluated [52-59]. In addition to increasing H₂ recovery, these processes would allow CO₂ to be captured to reduce the carbon intensity of H₂ production. However, conventional membranes do not have sufficient ability to separate CO₂ and H₂. Consequently, other separation technologies (absorption, cryogenic) would typically be preferred for PSA tail gas treatment.

3.2. Membrane processes for CO₂ capture from PSA tail gas

The recent development of high performance CO₂-selective membranes warrants the re-examination of membrane processes for CO₂/H₂ separation in PSA tail gas streams. Table 2 shows the gas separation properties of the membranes, which were obtained in the field tests described in Part I of this paper. A sample hybrid design using a combination of membrane and cryogenic processes is shown in Fig. 2. The cryogenic unit produces high-pressure liquid CO₂ ready for sequestration, while the membrane step selectively recycles CO₂ to enhance the CO₂ capture rate. Membrane-cryogenic hybrid processes have been practiced for liquid propylene recovery from purge gas streams containing propylene and N₂ [2,60], and they have also been explored for CO₂ capture from coal-fired power plant flue gas containing mainly CO₂ and N₂ [43,47,61-63].

Table 2

Separation properties of the CO₂-selective membrane used for process simulations. In the CO₂/H₂ sensitivity study, the H₂ permeance is varied, while the CO₂ permeance and the selectivity of H₂/CH₄ and H₂/CO remains the same.

Gas	Permeance (gpu)*	CO ₂ /gas selectivity	H ₂ /gas selectivity
Hydrogen	100	10	--
Carbon dioxide	1000	--	0.1
Methane	67	15	1.5
Carbon monoxide	67	15	1.5

* $1 \text{ gpu} = 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg}) = 7.501 \times 10^{-12} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$.

Parameter	① PSA Tail gas	② Liquid CO ₂	③ Membrane feed	④ CO ₂ recycle	⑤ H ₂ , CO & CH ₄
Composition (vol%)					
H ₂	36.1	0.6	38.0	20.7	71.7
CH ₄	3.0	0.3	2.7	1.1	5.8
CO	6.1	0.3	5.3	2.1	11.5
CO ₂	54.8	98.8	54.0	76.1	11.0
Flow (MMscfd)	32.8	16.4	48.2	31.9	16.4
Pressure (bar)	5	30	30	5	30

Fig. 2. Flows and compositions of the gas streams in a PSA tail gas treatment system using a membrane-cryogenic hybrid process. The tail gas is from a PSA unit producing 67.2 MMscfd H₂ (as shown in Fig. 1). The system captures 90% of the CO₂ as a high-pressure liquid ready for sequestration.

As shown in Fig. 2, the low-pressure PSA tail gas at 5 bar is compressed to 30 bar and cooled to -30°C. A portion of the CO₂ in the gas condenses and is removed as liquid CO₂. The remaining condenser off-gas is then sent to the membrane unit containing the CO₂-selective membranes. The bulk of the CO₂ in the condenser off-gas permeates the membrane and is recycled to the front of the compressor to be treated a second time. The gas leaving the membrane unit (⑤) consists of 72% H₂ and 11% CO₂; this gas, still at approximately 30 bar, is preferably mixed with the feed gas to the main reformer unit or used as fuel. Optionally, this stream may be treated to recover H₂ using a H₂-selective membrane. The H₂-rich permeate gas can be sent to the front of the PSA system to recover essentially all of the H₂ previously lost with the PSA tail gas. In this case, cheap natural gas would replace the H₂-rich tail gas as fuel for the reformer (although the carbon emissions for this case would be higher compared to using H₂ as fuel).

3.3. Optimal membranes for CO₂ capture from PSA tail gas

Fig. 3 shows the effect of CO₂ capture rate on the required membrane area and power consumption (for the compressor and refrigerator) for CO₂ capture from the PSA tail gas. The tail gas is from the PSA unit producing 67.2 MMscfd H₂, as shown in Fig. 1. In general, increasing the CO₂ capture rate increases the required membrane area and power consumption, and the rate of increase becomes much steeper when the required CO₂ capture rate is higher than ~60%. At these high capture rates a larger recycle stream from the membrane permeate to the front of the compressor is required, which increases the required membrane area and power consumption.

Fig. 3. Effect of CO₂ capture rate on the required (a) membrane area and (b) power consumption (including compressor and refrigerator requirements) for a CO₂ capture process. The membrane properties are recorded in Table 2.

Fig. 4 shows the effect of membrane CO₂/H₂ selectivity on the required membrane area and power consumption at different CO₂ capture rates. Increasing selectivity decreases the membrane area and power consumption. Above a membrane selectivity of about 8, there is little additional improvement in process performance. In general, the membrane separation performance is determined by the membrane properties and operating conditions such as the feed-to-permeate pressure ratio: higher membrane gas selectivities and higher feed-to-permeate pressure ratios increase the product purity [2,47]. In the process shown in Fig. 2, the feed-to-permeate pressure ratio is only 6. Therefore, when the membrane has relatively low CO₂/H₂ selectivity (especially less than 6), increasing the membrane gas selectivity has a significant impact on the separation performance. However, as the membrane CO₂/H₂ selectivity increases above 10, the membrane separation performance is mainly governed by the feed-to-permeate pressure ratio, and therefore, further increases in the CO₂/H₂ selectivity have minimal

improvement on the membrane system performance [2,46,47]. A higher pressure ratio could be used to take advantage of a high selectivity membrane, but the cost associated with the additional compression required to do this is prohibitive.

Fig. 4. Effect of membrane CO_2/H_2 selectivity on the required (a) membrane area and (b) power consumption for CO_2 capture from the PSA tail gas. The process simulations assume the membranes have CO_2 permeance of 1000 gpu with varying H_2 permeances, while the selectivities of H_2/CH_4 and H_2/CO remain the same, as shown in Table 2.

3.4. Cost of CO_2 capture from PSA tail gas

Table 3 shows the capital and operating costs of the membrane process (shown in Fig. 2) for CO_2 capture from the PSA tail gas at two CO_2 capture rates, 40% and 90%. The cost assumptions are shown in Table 1, and the membrane separation properties are shown in Table 2. Included in these calculations is the cost of CO_2 capture – a metric that includes capital and operating costs – which is frequently used to evaluate the cost of CO_2 removal technologies. The

Table 3 results demonstrate that compression and refrigeration costs dominate the capital and operating costs of CO₂ capture.

Table 3

Comparison of the cost of a hybrid membrane-cryogenic system for CO₂ capture from the PSA tail gas at different capture rates. The system design is shown in Fig. 2 with the compression of the entire feed stream, and cost assumptions are shown in Table 1.

System parameters	Units	CO ₂ capture rate	
		40%	90%
Membrane system information			
Membrane area	m ²	320	1750
Compressor power	MWe	4.2	5.9
Refrigerator power	MWe	0.9	1.7
Liquid CO ₂ produced	Tonnes/day	378	852
Total plant capital cost	\$MM	13.1	21.5
Membrane skid	\$MM	0.16	0.88
Compressor and refrigerator skid	\$MM	5.1	7.6
Bare erected plant	\$MM	8.4	13.8
Engineering fees	\$MM	0.8	1.4
Contingencies	\$MM	3.9	6.3
Annual operating cost	\$MM	4.3	6.7
Depreciation and interest	\$MM	2.0	3.2
Compressor and refrigerator power	\$MM	2.3	3.4
Module replacement	\$MM	0.01	0.06
Cost of liquid CO ₂ production	\$/tonne	36	25

Fig. 5(a) shows the effect of CO₂ capture rate on the cost of liquid CO₂ production. Initially, the cost of CO₂ capture decreases significantly with increasing CO₂ capture rate, before increasing when the CO₂ capture rate is above 80%. There seems to be an optimal CO₂ capture

rate at 80%, reflecting the compromise (trade-off) between the amount of liquid CO₂ produced and the power requirement of the compressor and refrigerator. At low CO₂ capture rate, the full stream still needs to be compressed and chilled, and therefore the cost of producing liquid CO₂ per tonne is very high. As the CO₂ capture rate increases, the amount of separated CO₂ increases faster than the compressor and refrigerator costs increase and therefore, the cost of liquid CO₂ production decreases. At CO₂ capture rates above 80%, any further increase in the CO₂ capture rate significantly increases the size of the CO₂ recycle stream, the power consumption, and hence, the cost of liquid CO₂ production.

Fig. 5. (a) Effect of the CO₂ capture rate on the cost of CO₂ capture (as a supercritical liquid) from the PSA tail gas using the membrane process design shown in Fig. 2 and the membrane separation properties shown in Table 2. (b) The effect of capture rate on CO₂ capture cost when only a portion of the tail gas is compressed and sent to the membrane process while the remaining gas bypasses the compression and CO₂ capture steps.

As a practical matter, once the tail gas is compressed as in the Fig. 2 design, it makes sense to capture CO₂ in this stream at a high rate. Otherwise, the energy spent compressing the CO₂ is wasted if this gas is left in the fuel gas residue stream. A better way to operate the system at low

capture rates is to compress only a portion of the tail gas stream, capture CO₂ at a high rate from this stream, and divert the rest of the tail gas stream to bypass the compression and CO₂ capture steps. Fig. 5(b) shows the results of this analysis where the capture rate for the stream sent to the membrane unit is fixed at 80% (the minimum cost on the Fig 5(a) curve). In this bypass scenario, the cost of capture with the membrane process on a \$/tonne basis is constant below 80%. Above this value, the full stream needs to be compressed, and the cost of capture increases as shown before in Fig 5a. In general, the overall cost of CO₂ capture from the PSA tail gas is in the range of \$20-30/tonne liquid CO₂, which appears competitive with conventional separation technologies proposed for capturing CO₂ from shifted syngas (~\$40/tonne CO₂) [6].

4. Membranes for CO₂ capture in the GE IGCC process

Several gasification technologies are available to produce syngas from coal. These processes have unique gasifier designs, which produce syngas at various combinations of pressures, temperatures and gas compositions. The membrane processes for CO₂ capture need to be integrated into the process trains to achieve the best possible energy efficiency.

The U.S. DOE has examined the economics of various separation technologies for CO₂ capture from coal-derived syngas produced using GE gasification technology [39]. The syngas is produced at ~50 bar and contains about 40% CO₂. The CO₂ is captured using Selexol, which consumes 50 MW_e for a GE IGCC plant with a power generation of 556 MW_e [39]. Selexol performance is the current standard against which any new pre-combustion CO₂ capture technology is measured, including membrane systems.

4.1. Membrane processes for CO₂ capture from the GE IGCC process

Fig. 6 shows a membrane design for H₂ purification and CO₂ capture from shifted, coal-derived syngas, using CO₂-selective membranes. Other membrane designs are possible, and may offer advantages, including ones using H₂-selective or combinations of membranes. However, here we will focus on the use of CO₂-selective membranes in the simple Fig. 6 design. The GE IGCC shifted syngas stream has a flow of 570 MMscfd and contains 56.4% H₂, 41.3% CO₂ and 2.3% CO/hydrogen sulfide/nitrogen/argon (on a dry basis) at 50 bar [35,39], which is the design basis for a power plant that generates 556 MWe of power. The stream conditions shown in Fig. 6 are based on a membrane with a CO₂ permeance of 1000 gpu and a CO₂/H₂ selectivity of 10.

Parameter	① Feed gas	③ H ₂ product	④ Permeate	⑤ Liquid CO ₂	⑥ CO ₂ recycle
Components (%)					
H ₂	56.4	90.4	34.6	1.6	63.6
CO ₂	41.3	6.7	64.1	96.9	35.1
CO	1.1	1.7	0.4	0.1	0.7
N ₂	0.7	1.1	0.1	0	0.2
H ₂ S	0.5	0.03	0.8	1.4	0.4
Flow (MMscfd)	570	353	468	220	249
Pressure (bar)	50	31	6.1	50	50

Fig. 6. Flow scheme and stream compositions of a membrane system to recover and separate H₂ and CO₂ from 570 MMscfd shifted GE IGCC syngas. The membrane separation properties used in the simulation are shown in Table 2.

As shown in Fig. 6, a single-step CO₂ separation unit partitions the feed gas into a high-pressure H₂-rich gas containing 90.4% H₂ (②) and a low-pressure CO₂-rich permeate containing 64.1% CO₂ (④). The H₂-rich gas can be used in a turbine to generate power, or if high-purity H₂ product is required, it can be sent to a PSA unit for final clean-up. Because the gas to the turbine is required at 31 bar (③), stream (②) can be sent first to a turbo-expander to recover energy (4.4 MW_e).

The CO₂-rich permeate (④) is sent to the CO₂ liquefaction unit, which uses about 16 MW_e of power to provide the required refrigeration. The liquefaction off-gas containing 35.1% CO₂ is recycled back to the front of the membrane system. The liquid CO₂ product stream (⑤), at 50 bar and containing 96.9% CO₂, can be easily pumped to injection pressure required for EOR or sequestration.

The overall result of the membrane process shown in Fig. 6 is 98.7% H₂ recovery in the product gas, and 90% CO₂ capture in the liquid CO₂ stream. The process uses about 41 MW_e of power for the compressor shown and a further 16 MW_e for the refrigeration plant needed to condense the liquid CO₂. Considering the energy (4.4 MW_e) recovered from the turbo-expander, the total energy use of the system is about 52.6 MW_e. The feed flow rate to this membrane system is equivalent to the quantity of syngas that would be used as feed to a 556 MW_e IGCC power plant. Thus, the energy use for H₂ purification and carbon capture (including liquefaction) corresponds to about 9.3% of the power produced from combustion of the H₂ product. These values show that the membrane liquefaction process using base case membrane properties is competitive with, but not better than Selexol on an energy use basis.

4.2. Optimal membranes for CO₂ capture from the GE gasification process

Fig. 7 shows the effect of CO₂ capture rate on the required membrane area and power consumption at two CO₂/H₂ selectivity values (10 and 20) achieved in lab tests described in Part I of this study. Increasing the CO₂ capture rate increases the power consumption and membrane area, and the rate of increase becomes steeper when the required CO₂ capture rate is more than ~60%. This is often expected for membrane processes, because the separation is driven by pressure differential. As the CO₂ capture rate increases, the CO₂ partial pressure in the syngas product decreases, leading to a significant reduction in the CO₂ partial pressure difference across the membrane, and thus increased requirements for membrane area and power consumption. There is discussion among industry and government sources that the near-term goal for CO₂ capture in coal power plants may be about 50% capture because such a capture rate makes the CO₂ emissions per kWh from coal plants about the same as that for natural gas combined cycle power plants. For this partial capture case, a membrane process may be particularly attractive.

Fig. 7. Effect of the CO₂ capture rate on (a) the required membrane area and (b) power consumption (including compressor and chiller requirements) for a GE IGCC process. The membrane properties are recorded in Table 2.

Fig. 7 also compares the membrane area and power consumption using membranes with CO_2/H_2 selectivities of 10 and 20. These two membranes are assumed to have the same CO_2 permeance, with varying H_2 permeances. Increasing the CO_2/H_2 selectivity from 10 to 20 seems to have negligible effect on the required membrane area, which is expected since the CO_2 permeance is the same for both membranes. On the other hand, higher CO_2/H_2 selectivity decreases the power consumption, especially at higher CO_2 capture rates. For example, at 90% CO_2 capture the power consumption of the membrane process is reduced by 20% (from 53 to 43 MWe) when the selectivity is increased from 10 to 20.

Fig. 8 shows the effect of membrane CO_2/H_2 selectivity on the required membrane area and power consumption for different CO_2 capture rates from a GE IGCC plant. Increasing selectivity decreases the membrane area and power consumption. Power consumption is particularly sensitive to the membrane selectivity at high capture rates. This is because high CO_2 capture rates require significant recycle of CO_2 back to the chiller by membrane permeation. If the membrane selectivity is relatively low, substantial H_2 will also permeate the membrane and then be recompressed, driving up energy consumption. Nevertheless, even at 90% capture, above a membrane selectivity of about 20, there is little additional improvement in process performance.

Fig. 8. Effect of the membrane CO_2/H_2 selectivity on the required (a) membrane area and (b) power consumption (including compressor and chiller requirements) for the GE gasification process. The membranes are assumed to have CO_2 permeance of 1000 gpu with varying H_2 permeances, while the H_2/CH_4 and H_2/CO selectivity remains the same, as shown in Table 2.

Fig. 9 compares the power consumption of the Fig. 6 membrane process and Selexol for CO_2 capture from the GE gasification syngas. In both cases, H_2 recovery and CO_2 capture rates are held constant at ~99% and 90%, respectively. The calculations show that with a membrane selectivity of 10, the power consumption of the membrane process is about equivalent to that of Selexol. At a membrane CO_2/H_2 selectivity of 20, the membrane process uses about 20% less energy. As discussed in Part I of this study [4], membranes with this type of performance have been demonstrated in the field tests treating real coal-derived syngas.

Fig. 9. Comparison of power consumption for a membrane process with different CO₂/H₂ selectivities and the Selexol process for CO₂ capture from the GE IGCC process. The membrane properties are shown in Table 2.

4.3. Cost of CO₂ capture from the GE gasification process

Fig. 10 shows the effect of CO₂ capture rate on the cost of liquid CO₂ production and the total capture plant cost for capture from a coal-derived syngas produced by a GE IGCC plant. The assumptions for the costs and membrane separation performance have been shown in Tables 1 and 2, respectively. The cost of CO₂ capture increases with increasing CO₂ capture rate, and the rate of increase accelerates above about 80% capture. This result reflects the larger recycle stream and larger membrane, compressor and refrigeration systems needed at higher capture rates. This behavior is different from that observed for CO₂ capture from the PSA tail gas (as shown in Fig. 5(a)), in which the cost of liquid CO₂ production initially decreases with increasing rates of CO₂ capture. This difference is due to the fact that the GE syngas is already at pressure, and therefore, the membrane capture process does not need a large feed compressor as in the case of the PSA tail gas.

Fig. 10. Effect of the CO₂ capture rate on the cost of liquid CO₂ production and total capture plant cost for CO₂ capture from the GE IGCC syngas. The process schematic is shown in Fig. 6, and the membrane separation properties are shown in Table 2.

Also shown in Fig. 10 is the total membrane capture plant cost, which increases regularly with increasing capture rate. At a CO₂ capture rate of 90%, the membrane-based plant cost is \$192 million (US). This value is lower than the cost for a Selexol unit (\$252 million) to perform the same CO₂ capture rate [39]. The cost of liquid CO₂ production using the membrane separation is in the range of \$15-20/tonne at 90% capture, which is significantly less than the costs for conventional separation/purification technologies processing the same type of gas (\$30-40/tonne CO₂) [6].

5. Membranes for CO₂ capture in the TRIGTM IGCC process

5.1. Background on the TRIG process

The Transport Integrated Gasification (TRIGTM) process has attracted significant interest in the last few years. Southern Company is currently constructing an IGCC power plant with CO₂ capture in Kemper County, MS, based on this technology. The Mississippi plant is one of only two commercial-scale plants under construction in the United States that use coal gasification for power production with CO₂ capture.

The TRIG process uses an air-blown gasifier. Among the advantages of this technology compared to other gasification processes are the avoid of the use of a large air separation unit, lower operating temperatures resulting in less expensive construction materials, and the capability to use less expensive low rank coals as feeds [64].

5.2. Membrane processes for CO₂ capture from the TRIG process

Fig. 11 shows a design layout for membrane-based CO₂ capture from an air-blown IGCC power plant. The design and simulation of this process assume the gas to be treated is a high-pressure H₂-rich syngas stream exiting a low-temperature shift reactor. For the simulations, the gas stream exiting the shift reactor has a flow of 2,000,000 lb/hr and contains 25.1% H₂, 23.4% CO₂, 48.8% N₂ and 2.7% CO/hydrogen sulfide/methane/argon (on a dry basis) at 23.8 bar (equivalent to the shift reactor flow for a 600 MW_e power plant) [64].

Parameter	① Feed gas	② Membrane feed	③ H ₂ product	④ Permeate	⑤ Liquid CO ₂	⑥ CO ₂ recycle
Components (%)						
H ₂	25.1	24.7	29.6	18.7	0.3	23.9
CO ₂	23.4	35.0	9.7	65.8	98.8	56.4
CO	0.9	0.8	1.1	0.5	0	0.7
CH ₄	1.8	1.6	2.1	1.0	0.1	1.3
N ₂	48.8	37.9	57.5	14.0	0.8	17.7
Flow (MMscfd)	728	1120	616	504	112	392
Pressure (bar)	23.8	23.8	23.8	4.4	23.8	23.8

Fig. 11. Simulation flow scheme and stream compositions of a membrane system to separate H₂ and CO₂ from the shifted IGCC syngas produced in an air-blown gasifier, such as that used in the TRIG process. The process captures 65% of the CO₂ in liquid form, ready for sequestration.

As shown in Fig. 11, a one-step CO₂ separation unit partitions the feed gas into a high-pressure H₂-rich gas containing 29.6% H₂ (stream ③) and a low-pressure CO₂-rich permeate containing 65.8% CO₂ (stream ④). The H₂-rich gas can be used in a turbine to generate power. The CO₂-rich permeate is sent to a CO₂ liquefaction unit, which uses about 20 MW_e of power to provide the refrigeration required. The liquefaction off-gas containing 56.4% CO₂ is recycled back to the front of the membrane system (stream ⑥). The liquid CO₂ product stream (⑤) is at 23.8 bar and contains >98% CO₂, which is ready for pumping to utilization or sequestration sites.

The overall result of the membrane process shown in Fig. 11 is 99.8% H₂ recovery in the product gas, and 65% CO₂ capture in the liquid CO₂ stream. The process uses about 37 MW_e of power for the compressor shown and a further 20 MW_e for the refrigeration plant needed to condense the liquid CO₂. The total energy use of the system is about 57 MW_e. The feed flow rate to this membrane system is equivalent to the quantity of syngas used by a 600 MW_e IGCC power plant. Thus, the energy use for H₂ purification and carbon capture corresponds to about 9.5% of the power produced from combustion of the H₂ product.

5.3. *Optimal membranes for CO₂ capture from the TRIG process*

Fig. 12 shows the effect of CO₂ capture rate on the required power consumption and the membrane area for CO₂ capture from a TRIG-type process. As in previous cases, increasing the CO₂ capture rate increases the power consumption and membrane area, and the rate of increase becomes much steeper when the required CO₂ capture rate is more than ~60%. Increasing CO₂/H₂ selectivity from 10 to 20 has negligible effect on the required membrane area, and decreases the required power consumption, especially at higher CO₂ capture rates.

Fig. 12. Effect of the CO₂ capture rate on (a) the membrane area and (b) power consumption (including compressor and chiller requirements) required for CO₂ capture from a TRIG-type process. The process simulations assume the membranes have CO₂ permeance of 1000 gpu and varying H₂ permeances.

Fig. 13 shows the effect of membrane CO₂/H₂ selectivity on the required membrane area and power consumption at different CO₂ capture rates. Increasing selectivity decreases the membrane area and power consumption. Above a membrane selectivity of about 20, there is little additional improvement in the process energy consumption. On the other hand, higher selectivities generally mean lower membrane permeances, which translate to higher membrane area requirements, as shown in Fig. 13(a).

Fig. 13. Effect of the membrane CO_2/H_2 selectivity on the required (a) membrane area and (b) power consumption (including compressor and refrigerator requirements) for a TRIG-type gasification process. The process simulations assume the membranes have CO_2 permeance of 1000 gpu with varying H_2 permeances.

5.4. Cost of CO_2 capture from TRIG process

Fig. 14 shows the effect of CO_2 capture rate on the total plant capital cost and the cost of liquid CO_2 production from coal-derived syngas produced in TRIG plants. The cost assumptions and membrane separation performance have been shown in Tables 1 and 2, respectively. Both total plant capital cost and the cost of CO_2 capture increase with increasing CO_2 capture rate because a higher CO_2 capture rate requires a larger recycle stream and larger membrane, compressor and refrigeration systems. The degree of increase becomes steeper as the CO_2 capture rate increases above 60%. This behavior is similar to that observed for CO_2 capture from GE gasifier syngas, as shown in Fig. 10.

Fig. 14. Effect of the CO₂ capture rate on the cost of liquid CO₂ production and the total plant capital cost for capture from a TRIG gasifier syngas using the membrane process schematic shown in Fig. 11.

Compared to the GE gasifier case, both the cost of liquid CO₂ production and the capture plant cost are higher for the TRIG gasifier. For example, the membrane capture plant capital cost is about \$220 million at CO₂ capture rate of 65% for the TRIG gasifier, compared to only \$192 million for 90% CO₂ capture from a GE IGCC process [39]. Similarly, the cost of liquid CO₂ production at a similar capture rate is significantly higher for the TRIG process. As discussed below, presumably this cost difference is related to the different CO₂ concentration and partial pressure in the syngas fed to the membrane capture process.

While the cost of CO₂ capture from the TRIG syngas process may be relatively high (compared to the GE syngas process), the cost of the gasification process itself must also be considered. For example, the TRIG IGCC process uses air, instead of pure oxygen, and therefore, it avoids the cost of an expensive air separation unit, which is a significant capital and operating cost in the GE IGCC process [39].

6. Comparison of CO₂ capture cost using membranes in the three processes

Fig. 15 compares the cost of liquid CO₂ production using membranes for the three processes examined in this paper: a 67.2 MMscfd H₂ production plant, a 556 MW_e GE IGCC facility, and a 600 MW_e TRIG IGCC process. The economics of the membrane process vary markedly depending on the process and operating conditions.

Fig. 15. Comparison of the cost of liquid CO₂ production using CO₂-selective membranes from three processes: a TRIG power plant (600 MWe or 728 MMscfd syngas), a H₂ plant (with 32.8 MMscfd PSA tail gas feed) and a GE IGCC plant (556 MWe or 570 MMscfd syngas). The results have been shown in Figs. 5, 10 and 14.

Of the cases examined, CO₂ capture via membranes from the GE gasification process has the lowest liquid CO₂ production cost. This result is primarily related to the relatively high CO₂ partial pressure in the shifted syngas produced by the GE process. For example, Table 4 compares the CO₂ partial pressure in the syngas fed to the membrane process and the cost of capture at 90% CO₂ removal for the different cases. Comparing the two gasification processes, the ratio of the syngas CO₂ partial pressures (GE:TRIG = 20.7/5.6 = 3.7) is almost the inverse of

their capture costs at 90% capture ($\text{TRIG:GE} = \$63/\$16.7 = 3.8$). This general dependence of capture cost on CO_2 partial pressure is typical for separation technologies, and is particularly true in the case of membrane systems, which are known to be most competitive when the partial pressure of the gas to be removed is high.

Table 4.

Comparison of the syngas feed conditions and liquid CO_2 production costs.

Process	Feed pressure (bar)	Feed CO_2 content (%)	Feed CO_2 partial pressure (bar)	Liquid CO_2 production cost at 90% capture (\$/tonne)
Hydrogen production	5	54.8	2.7	25.2
GE IGCC	50	41.3	20.7	16.7
TRIG IGCC	23	23.4	5.6	63.0

As shown in Table 4 and Figure 15, the cost of membrane-based CO_2 capture from H_2 production (PSA tail gas) is intermediate between the two gasifier cases (higher than GE, but lower than TRIG). This finding is interesting because the feed CO_2 partial pressure for the PSA tail gas (2.7 bar) is lower than the TRIG syngas (5.6 bar), which would suggest a higher cost to treat the PSA tail gas. The reason that this is not the case is likely due to the higher CO_2 concentration in the PSA tail gas (54.8%) relative to TRIG syngas (23.4%), and the nature of the hybrid membrane-cryogenic capture processes used. Liquefaction of CO_2 requires a gas stream with relatively high CO_2 concentration, for example, higher than about 56% at -30°C and 23.8 bar (as shown in Fig. 11). If the feed gas to the capture process contains low CO_2 concentration, such as for the TRIG syngas, high flow rates of recycled permeate (enriched in CO_2) are required for mixing with the feed gas so that the gas entering the liquefaction step has sufficient CO_2

content to produce liquid CO₂. This drives up the cost of capture for dilute feed streams like TRIG syngas. In contrast, the PSA tail gas is relatively concentrated, making liquefaction easier and less costly.

7. Conclusions

Membrane process designs based on CO₂-selective Polaris membranes are evaluated for H₂ purification and CO₂ capture from the PSA tail gas produced in H₂ production plants, and from the syngas produced by two gasification processes: the GE and TRIG technologies. The performance of the hybrid membrane-cryogenic process varies markedly depending on the membrane separation properties, process stream conditions and the targets of CO₂ capture rate.

- (1) In the H₂ production plant, increasing the CO₂ capture rate increases the required membrane area and power consumption, and the rate of increase becomes much steeper when the required CO₂ capture rate is more than ~60%. Because the PSA tail gas must be compressed before being fed to the CO₂ capture system, it is most economical on a \$/tonne basis to capture a high percentage of the CO₂ (~80%). If lower capture rates are desired, a process bypass scenario would be used. Increasing CO₂/H₂ selectivity decreases power consumption and CO₂ capture cost. However, when the simulated membrane selectivity is above 10, any further increase in selectivity does not have significant effect on the power consumption.
- (2) For CO₂ capture from the syngas produced in the GE gasification process, increasing CO₂ capture rate significantly increases the energy consumption and the required membrane area, especially when the assumed CO₂ capture rate is above 80%. The power consumption of the membrane-based units decreases with increasing CO₂/H₂ selectivity. Membranes with CO₂/H₂ selectivity of 10 can capture 90% CO₂ with an energy consumption that is similar to

the energy required by the conventional SelexolTM process. With a membrane CO₂/H₂ selectivity of 20, the membrane-based process uses about 20% less energy than Selexol. Additional increases in selectivity have a relatively small effect on the power consumption.

(3) In 600 MW_e power plant TRIG process simulations, membranes with CO₂/H₂ selectivity of 10 are required to capture 65% CO₂ with an energy consumption of 57 MW_e. At higher capture rates, the cost increases dramatically for this dilute syngas feed. Increasing selectivity decreases the power consumption and capture cost. However, at a CO₂/H₂ selectivity above 20, any further increase does not have much impact on the energy consumption, while increasing the required membrane area.

In comparing CO₂ capture from the different processes, it seems capture cost depends on both the CO₂ partial pressure and concentration in the feed streams. Higher CO₂ partial pressure, such as that found in the GE IGCC syngas, will reduce the cost of capture. However, the capture cost does not scale only with partial pressure for the cases examined. Because hybrid membrane-cryogenic capture processes were used in this study, the concentration of CO₂ in the feed stream also has an impact on capture cost. Higher CO₂ feed concentration, such as that found in PSA tail gas, makes CO₂ liquefaction easier, and thus reduces the capture cost.

Based on the field tests described in Part I of this study and the design calculations presented here, CO₂-selective Polaris membranes show promise for CO₂ capture from reforming and gasification processes. Looking forward, further scale-up activities will be critical to establishing the reliability of membrane technology, and for confirming process economics of increasingly larger operations, using a broader array of possible process designs.

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