

FIELD TESTS OF MTR MEMBRANES FOR SYNGAS SEPARATIONS: Final Report of CO₂-Selective Membrane Field Test Activities at the National Carbon Capture Center

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EXECUTIVE SUMMARY

Syngas operations require separation of CO_2 and hydrogen for hydrogen production at refineries and petrochemical plants, and potentially for combined hydrogen production and CO_2 capture at integrated gasification combined cycle (IGCC) power plants. Membranes that selectively permeate CO_2 have attracted significant interest, because the purified hydrogen is retained at high pressure, thus avoiding costly downstream recompression. In this work, PolarisTM thin film composite membranes were evaluated for CO_2 removal from syngas. These membranes are highly permeable to CO_2 and reject the other major components of syngas, including hydrogen, carbon monoxide and methane.

This report describes the three-stage development of Polaris membranes for CO_2/H_2 separation, including: laboratory parametric tests of membrane stamps using pure- and mixed-gas streams, bench-scale tests of membrane modules using real syngas at a coal-fired gasification plant, and field demonstration of a membrane system producing liquid CO_2 . The gasification plant where the field tests were conducted is at the National Carbon Capture Center (NCCC) in Wilsonville, AL. The initial bench-scale test was conducted during the R03 gasifier campaign in November 2009 and Polaris modules were tested on either the bench-scale or small pilot field demonstration skid for all subsequent gasifier campaigns ending with the R11 campaign in August 2013. Cumulative run time on the bench-scale membrane module system was 4,400 hours, while the small pilot field demonstration skid had 800 hours of run time.

Early testing of MTR Polaris membrane modules on the bench-scale unit demonstrated CO_2 enrichment from 10% in the feed to 40 to 50% in the permeate in a single stage. Membrane and module improvements resulted in higher selectivity, which increased CO_2 purity to >50% for the same conditions in later tests. The 500 lb/hr small pilot skid was installed and commissioned successfully in December 2012. The system operated stably with commercial-sized modules and demonstrated liquid CO_2 production. During the last test campaign for the small pilot unit (R11), the system operated for over 400 hours producing >95% purity liquid CO_2 at a rate of up to 40 lb/hr.

CO₂-Selective Membrane Field Test Activities at the National Carbon Capture Center

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INTRODUCTION

Hydrogen is an important chemical in petroleum refining, ammonia synthesis and methanol synthesis. With annual production of 53 million metric tons worldwide, the hydrogen market was valued at \$88 billion in 2010 [1]. Currently, hydrogen is produced principally by steam reforming of hydrocarbons such as methane, followed by the water-gas shift reaction:

$$C_m H_n + H_2 O \to \text{mCO} + \frac{n+2m}{2} H_2 \tag{1}$$

$$CO + H_2O \to CO_2 + H_2 \tag{2}$$

The produced hydrogen inevitably contains impurities such as CO_2 , which typically need to be removed for hydrogen to be used further, as shown in Figure 1 [2]. The CO_2 is usually removed using pressure swing adsorption (PSA) technology, which produces high-purity hydrogen at high pressures. However, the PSA systems usually attain only 75-85% hydrogen recovery [3]. Considering the enormous amount of hydrogen made annually, any improvement in CO_2/H_2 separation efficiency would lead to significant hydrogen production savings.



Figure 1. Simplified process flow diagram for hydrogen or energy production from gasified or reformed fossil fuels.

Hydrogen has also attracted attention as a clean energy carrier for power production, often starting from coal, an especially abundant source of fossil energy in the U.S. and China [4]. In this application (also shown in Figure 1), coal is gasified to produce syngas. Ultimately the syngas is sent to a combustion turbine and the waste heat from gasification and syngas combustion is used to power steam turbines. The process is called Integrated Gasification Combined Cycle (IGCC). The syngas may be shifted and treated to remove CO_2 prior to combustion to avoid emission of this greenhouse gas. Because the CO_2 in syngas is relatively concentrated and at high pressure, CO_2 capture is easier in the pre-combustion IGCC approach than from post-combustion flue gas, which is typically at atmospheric pressure and contains only 4-13% CO_2 [5]. When costs of carbon capture are included, IGCC power production is believed to be less costly than power generated by direct combustion of coal [5, 6].

The current leading technologies for CO_2 capture from shifted syngas are physical absorption processes, such as SelexolTM or Rectisol[®][2]. These processes have a number of drawbacks [2, 4]. For example, the size of the absorption units is usually proportional to the amount of CO_2

being removed: post-shift syngas contains CO_2 at concentrations up to 45%, and therefore would require large and complex absorption systems for CO_2 removal. These absorption systems consume large amounts of energy in the absorber-stripper operation, and as a result, more efficient ways of separating CO_2 from the shifted syngas are widely sought.

Membranes offer an alternative approach for CO_2 capture and hydrogen purification at hydrogen production facilities and IGCC power plants due to their simplicity of operation and potentially high energy efficiency [4,5]. Both H₂-selective membranes [7-13] and CO_2 -selective membranes [14-26] have been explored. CO_2 -selective membranes are of interest for CO_2/H_2 separations in steam methane reforming – where it is desirable to leave the purified hydrogen at high pressure by permeating CO_2 from the syngas [14-20], in air-blown gasification processes – where CO_2 should be removed from syngas containing H₂ and N₂, and in oxygen-blown IGCC operations – where a combination of H₂-selective membranes for bulk hydrogen recovery and CO_2 -selective membranes for CO_2 purification and liquefaction could be a low-cost CO_2 capture process [5].

The development of Polaris CO_2 -selective membranes for hydrogen purification and CO_2 capture involved three stages of membrane evaluation, as shown in Figure 2.

- 1. First, the Polaris membranes with promising CO_2/H_2 separation properties were tested in the laboratory to understand the effect of operating parameters (including feed gas pressure, temperature and composition) on separation performance. Membrane stamps of 30 cm² were mounted in permeation cells [as shown in Figure 2(a)] for testing with pure and mixed gases. Most of this work was conducted at MTR in Newark, CA.
- 2. Secondly, the membranes were fabricated into semi-commercial spiral-wound modules containing $1 4 \text{ m}^2$ membrane area [as shown in Figure 2(b)] and tested on a bench-scale membrane skid treating a real syngas feed up to 50 lb/hr from a coal gasification plant at the National Carbon Capture Center (NCCC), in Wilsonville, AL.
- 3. Finally, a membrane-based small pilot demonstration system was constructed to process 500 lb/hr syngas (equivalent to a 0.15 MW_e IGCC power plant) and produce liquid CO₂ at NCCC. The demonstration unit used commercial-scale membrane modules (8-inch diameter, each containing about 20 m² of membrane area), as shown in Figure 2(c).



(a) Stage I: Laboratory test (permeation cell)





(c) Stage III: Small pilot system demonstration (commercial module)



Figure 2. Three test stages of Polaris membrane development for treating syngas. (a) A laboratory test of membrane stamps (0.0030 m^2) using permeation cells; (b) a bench-scale field test of spiral-wound modules (1 m in length and 4-inch diameter), each containing $1 - 4 \text{ m}^2$ membrane area; (c) a CO₂ liquefaction small pilot system demonstration, using commercial-scale spiral-wound modules (1 m in length and 8-inch diameter), each containing about 20 m² membrane area.

Membrane and Module Preparation

Established laboratory methods and commercial approaches were used to provide the membranes and modules required for testing at NCCC. A schematic of a typical industrial thin film composite membrane (such as Polaris) used for CO_2/H_2 separation is shown in Figure 3 [27]. Figure 4 shows an exploded view of a conventional cross-flow spiral-wound module for gas separation with three ports (feed, residue and permeate) [28].



Figure 4. Exploded view of a conventional spiral-wound membrane module (in cross-flow mode) for gas separation [28, 29].

Field Test at the NCCC

Syngas Production

NCCC operated a coal gasifier based on the Transport Integrated Gasification (TRIGTM) process at Wilsonville, AL [30, 31]. The TRIG process is expected to have lower capital and operating costs than other gasification processes because of its lower operating temperature, resulting in

less expensive construction materials, and the capability of using less expensive, low rank coals [30]. The gasifier at NCCC is usually operated in air blown mode and often fed with Powder River Basin (PRB) coal or lignite, producing as much as 20,000 lb/hr syngas, equivalent to the output of a 6 MW_e IGCC power plant [31].

Figure 5 shows the layout of the NCCC facility for the evaluation of syngas conditioning and CO_2 capture technologies at various levels of process maturity. Typical syngas conditions from PRB coal are recorded in Table 1. The raw syngas contains about 10% CO_2 and 10% hydrogen, with N₂ accounting for the bulk of the remainder due to the use of air in the gasifier. The syngas also contains high-boiling-point aromatic hydrocarbons (tars). The NCCC is able to provide a range of syngas flow rates (from 5 lb/hr to 1,000 lb/hr) as needed for the evaluation of various technologies. The raw syngas can be sent to a water-gas shift reactor to convert most of the carbon monoxide to hydrogen and CO_2 . The typical composition of post-shifted syngas is included in Table 1. NCCC is equipped with the necessary analytical instruments for real-time analysis and monitoring [31].



Figure 5. Layout of the gasification facility and the MTR membrane units at the NCCC for the evaluation of technologies at various levels of process maturity [32]. The syngas feed produced from the gasifier may be treated to remove sulfur and tar components before entering the membrane skid. tpd: ton/day; pph: lb/hr; T.O.: thermal oxidizer.

Operating Conditions	Raw Syngas	Shifted Syngas
Flow rate (lb/hr)	20,000	1,000
Pressure (bar)	13.4	13.4
Temperature (°C)	230	230
Water	Saturated	Saturated
Tars (aromatic hydrocarbons)	Saturated	Saturated
Gas Composition (dry vol %)		
H ₂	7.3	15.4
N ₂	73.0	65.8
CH ₄	1.2	1.2
CO	9.3	1.1
CO ₂	9.2	16.5
H ₂ S	100-400 ppm	100-400 ppm

Table 1. Typical Syngas Stream Conditions at the NCCC Gasification Plant.

Bench-Scale Membrane Skid

A bench-scale membrane skid was constructed and installed at NCCC in 2009 to test the separation performance of Polaris membrane modules for CO_2 removal from the real coal-derived syngas. Figure 6(a) shows a photo of the skid, which can accommodate one or two 4-inch-diameter membrane modules, each containing 1-4 m² membrane area. Figure 6(b) shows the simplified process flow diagram for the membrane skid. After pretreatment (including syngas cooling and tar scrubbing), the syngas near ambient temperature enters the membrane skid. After separation, the CO_2 -lean residue gas and CO_2 -rich permeate gas streams are measured, re-combined, and sent as one stream to the thermal oxidizer (T.O.) at NCCC.

For the bench-scale field test, the syngas flowed through the membrane skid at rates between 10 lb/hr and 50 lb/hr at feed pressures up to 13.4 bar. The temperature, pressure, and flow rate of the feed and permeate gas streams were measured using gauges on the skid. The residue stream flow rate was calculated based on the mass balance. Gas compositions were determined using a Siemens gas chromatograph at NCCC. Mixed-gas permeances were calculated and were also confirmed using the process simulation package, ChemCad 6.3.



Figure 6. (a) Photograph and (b) process flow diagram of the bench-scale membrane skid installed at NCCC that can treat up to 50 lb/hr syngas. The system can accommodate up to two 4-inch modules with a total membrane area of 2-8 m². FM: flow meter; P: pressure gauge.

Pilot Membrane Demonstration System for Liquid CO₂ Production

After the successful bench-scale testing of Polaris membrane modules, a small pilot demonstration system was designed and built in 2012. This system was designed to test a membrane-assisted CO₂ liquefaction process. Figure 7 shows a process flow diagram of the small pilot membrane demonstration system, which was designed to treat 500 lb/hr of coal-derived syngas, equivalent to the syngas output of a 0.15 MW_e IGCC power plant. Before entering the membrane system, the syngas was pretreated to remove sulfur compounds [including hydrogen sulfide (H₂S) and carbonyl sulfide (COS)] to less than 1 ppm, sent to a water quench tank and scrubber to remove tars, and then cooled to 10 °C. Two zinc oxide beds were used to remove residual H_2S and COS, avoiding their co-liquefaction in the liquid CO_2 condenser of the membrane system, and the tars were removed to prevent tar build-up and blocking of the valves or pipes in the system.

As shown in Figure 7, the small pilot membrane demonstration system consists of a two-stage membrane separation and condensation unit for CO_2 liquefaction [5]. The first membrane stage can accommodate one or two commercial-sized 8-inch-diameter modules with a total membrane area of 20-40 m², and the second membrane stage holds one or two 4-inch-diameter modules with a total membrane area of 3-6 m^2 . The syngas at 12.7 bar is heated to 20°C and passes to the first stage membrane, which concentrates CO_2 from 10% in the feed to 30-40% in the permeate. The hydrogen-enriched residue, which would typically be the product in a commercial system, is sent to the thermal oxidizer at NCCC. The CO₂-rich permeate stream is treated to remove H₂S and water vapor, compressed to 30 bar, and cooled to -30°C to condense out liquid CO₂. The overhead stream from the condenser is heated and sent to the second-stage membrane. The CO₂lean gas (containing 10% CO₂) from the second-stage membrane is sent to the thermal oxidizer, and the CO₂-rich gas (containing ~70% CO₂) from the second stage is recycled to the front of the compressor. The overall system captures 70% of the CO₂ in the feed as a high-pressure,

high-density fluid ready for sequestration.



Figure 7. A simplified process flow diagram of the small pilot membrane demonstration system constructed by MTR for capturing CO₂ from 500 lb/hr coal-derived syngas at NCCC. T.O.: thermal oxidizer.

The small pilot membrane demonstration system has three skids: a membrane skid, a compressor skid and a chiller skid. Figure 8 shows the general arrangement drawing of the entire membrane demonstration system. The skid size is 25 feet (length) by 25 feet (width) by 12.5 feet (height).



Figure 8. A general arrangement drawing of the 500 lb/hr syngas small pilot membrane demonstration system installed at NCCC.

Figure 9 shows photos of the three skids that make up the small pilot membrane demonstration system, before and after installation at NCCC. Figures 9(a) and 9(b) show photos of the membrane skid that enriches CO_2 from the raw syngas. The membrane skid contains two module housings, one sulfur removal vessel and two dryer vessels. Figure 9(c) shows the compressor skid, which can compress the syngas from about 1 bar to as high as 30 bar. Figure 9(d) shows the chiller package, which includes the chiller that cools the syngas to -30°C and the condenser that is used for CO_2 liquefaction. Figure 9(e) shows the layout plan for the system installation, and Figure 9(f) shows the complete small pilot membrane demonstration system installed at the site.

(a) Membrane skid

(b) Module housings on the membrane skid





(d) Chiller and CO₂ condenser



(e) NCCC site preparation for the system



(f) The MTR pilot demo system installed at NCCC



Figure 9. Photos of the 500 lb/hr syngas small pilot membrane system: (a) membrane skid; (b) membrane module housings on the membrane skid; (c) compressor; (d) chiller and CO₂ condenser; (e) site preparation for the demonstration system at NCCC; and (f) installed pilot membrane system at NCCC.

(c) Compressor

RESULTS AND DISCUSSION

Laboratory Testing of Polaris Membranes Conducted at MTR

Pure-Gas Permeation Properties

PolarisTM membranes, comprised of a proprietary polymer as the selective layer, have been designed for optimized CO_2/H_2 and CO_2/N_2 separation properties. Optimal membranes for CO_2/H_2 separation should have high CO_2 permeance to reduce the required membrane area and capital cost, and high CO_2/H_2 selectivity to increase the product CO_2 purity. Figure 10 presents a permeance/selectivity map for CO_2/H_2 separation in polymeric membranes at 25°C [33-35]. This type of plot was popularized by Robeson [33, 34]. Each point represents the separation properties for one particular polymer. The upper bound line in the figure gives a rough estimate of the highest selectivity possible for a given permeability in polymer-based materials [35]. The upper bound for CO_2/H_2 separation shows a positive slope; that is, materials with higher CO_2 permeance often have higher CO_2/H_2 selectivity as well [15].



Figure 10. Comparison of a Polaris membrane with other polymeric membranes in the literature (with assumed 1 µm-thick selective layer) used for CO₂/H₂ separation. Pebax/PEG [36]; PEGDA/PEGMEA [37]; PEO/PDMS [38]; PEGMEA + particles [39].

Polaris membranes show CO_2/H_2 separation performance close to the upper bound (CO_2 permeance of 2,000 gpu, and CO_2/H_2 selectivity of 10 at 25 °C). Decreasing temperature decreases CO_2 permeance and increases CO_2/H_2 selectivity of the Polaris membranes, providing great flexibility in the combinations of CO_2 permeance and CO_2/H_2 selectivity that can be produced.

Figure 10 also compares Polaris membranes with other membrane materials developed for CO_2/H_2 separation, which contain mainly poly(ethylene oxide) components, such as Pebax/PEG [36], PEGDA/PEGMEA [37], PEO/PDMS [38], and PEGMEA + particles [39]. The Polaris membranes show good combinations of CO_2 permeance and CO_2/H_2 selectivity, compared to these other membrane materials. Additionally, the Polaris membranes have been produced at commercial scale for the field tests.

Mixed-Gas Separation Properties

Various Polaris membranes were tested with gas mixtures to understand the effect of operating conditions on mixed-gas CO_2/H_2 separation properties. Figure 11 shows the mixed-gas permeances and selectivities at various feed gas compositions, temperatures and pressures for a membrane stamp that showed pure-gas CO_2 permeance of 1,300 gpu and CO_2/H_2 selectivity of 12 at 4.4 bar and 20°C.

Despite the somewhat complex behavior shown in Figure 11, it is clear that at 0°C and -20°C, the membrane stamp showed mixed-gas CO_2/H_2 selectivity of more than 10, which was a target identified by a separate process simulation and economic analysis. In addition, the presence of nitrogen in the feed gas (at 0, 20, or 40%) seems to have minimal effect on the mixed-gas CO_2/H_2 separation properties.





Figure 11. Effect of temperature and pressure on the mixed-gas separation properties of a Polaris membrane stamp. (a) Mixed-gas CO_2 permeance and (b) CO_2/H_2 selectivity with a 20:40:40 (CO_2 :H₂:N₂) feed; (c) mixed-gas CO_2 permeance and (d) CO_2/H_2 selectivity with a 60:20:20 (CO_2 :H₂:N₂) feed; (e) mixed-gas CO_2 permeance and (f) CO_2/H_2 selectivity with an 80:20 (CO_2 :H₂) feed.

Bench-Scale Test of Polaris Membrane Modules

The gasifier plant at NCCC operates on a campaign basis with a total operating time of approximately 2,000 hours per year. There are 1-3 campaigns per year with each campaign lasting 500 - 1,000 hours. The Polaris membrane modules were tested for CO₂ removal from syngas using the bench-scale skid (shown in Figure 6), starting with the third gasifier campaign

(R03) in 2009 and continuing through gasifier run R10 in Spring 2013. The following chart summarizes the type of membrane tested and equipment changes/improvements implemented in each of the bench-scale runs. The hours listed in Table 2 represent the anticipated time of syngas availability for each campaign. Over the duration of all of the test campaigns, MTR Polaris membranes on the bench-scale system processed syngas for 4,400 hours.

Table 2.General Descriptions of Membrane Syngas Performance Tests Run Using an
MTR Membrane Separation Bench-Scale Skid for Polaris Membrane Testing
During Syngas Campaigns at NCCC from September 2009 through April 2013.

Campaign Designation, Test Time and Dates	Feed Flow Rate (lb/hr)	Membrane Selections Tested and Skid Changes	
R03 (500 hrs) 11/17/2009-12/10/2009	10	Lower flux membrane	
R04 (500 hrs) 04/03/2010-04/28/2010	25	Higher flux membrane	
R05 (750 hrs) 08/02/2010-09/03/2010	25	Improved tar scrubber system; installation of heat tracing in the membrane skid	
R06 (1,000 hrs) 07/2011-08/2011	50	Improved tar scrubber system using cooled water	
R07 (1,000 hrs) 10/2011-12/2011	50	New membrane configurations; two modules in series installed in the vessel	
R08 (1,000 hrs) 06/2012-07/2012	50	New membrane configurations; two modules in series installed in the vessel	
R09 (500 hrs) 12/3/2012-12/19/2012	50	New membrane configurations; one module installed in the vessel	
R10 (750 hrs) 3/21/2013-4/20/2013	50		

CO₂ Removal

During the NCCC gasifier R03 run (November 17, 2009 to December 10, 2009), the raw syngas (with a flow rate of 10 lb/hr) was sent to a water-gas shift reactor and then passed through a desulfurization unit to remove sulfur components (H_2S and COS) to less than 10 ppm. The shifted syngas was then fed to a water cooler/condenser to remove tars, and cooled to near ambient temperature. The typical shifted syngas stream conditions entering the bench-scale test unit were provided earlier in Table 1.

Figure 12 shows the Polaris membrane module performance for CO_2 removal from syngas during approximately 20 days of continuous operation with a single bench-scale module. The feed temperature fluctuated between $-5^{\circ}C$ and $25^{\circ}C$ during the field test, mainly due to changes in the ambient temperature. Figure 12(a) shows that the Polaris membrane module can enrich CO_2 content, from 10-12% in the feed to 40-60% in the permeate. The performance was stable during the entire period of operation, indicating that there was no aging or performance deterioration of the membrane module after exposure to the shifted desulfurized syngas.

Figures 12(b) and 12(c) show mixed-gas permeances and mixed-gas CO_2/gas selectivities for the module as a function of time. In general, the Polaris membrane module shows CO_2 permeance of 100-300 gpu, CO_2/H_2 selectivity of 6-10, CO_2/CO selectivity of 10-20, and CO_2/N_2 selectivity of 20-50. It should be noted that a relatively low permeance Polaris membrane module was prepared for this test to control the stage-cut in the experiment to less than 15%. If a high permeance Polaris module were used with the available syngas feed flow rate, most of the feed gas would permeate the module. Overall, the important result from this test is that the module performance was stable with time.



Figure 12. Operating the bench-scale membrane module test skid: Polaris membrane module performance as a function of time during a test period of about 20 days. (a) CO_2 concentration in the feed and permeate streams; (b) mixed-gas permeances for CO_2 , H_2 , CO and N_2 and (c) mixed-gas CO_2 /gas selectivities. Feed gas composition is similar to that shown in Table 1.

H₂S Removal

In another gasifier campaign (R06 run from July 11 to August 20, 2011), the sulfur components were not removed before entering the membrane bench-scale skid. The syngas compositions were similar to that in Table 1, but with an H₂S content of 320 ppm. Figure 13 shows the H₂S/CO₂ selectivity in the module at 32°C as a function of time. The Polaris membranes showed

 H_2S/CO_2 selectivity of around 3, consistent with rubbery polymers where separation is determined by the solubility selectivity. H_2S with a critical temperature of 373 K is more condensable than CO_2 with a critical temperature of 304 K, and therefore, H_2S has higher solubility and permeability than CO_2 . The field test with syngas containing H_2S shows that the membrane module is stable in the presence of H_2S . Thus, Polaris membranes also provide one way to co-capture H_2S and CO_2 , if co-sequestering of H_2S and CO_2 is possible [5]. Because H_2S is more permeable than CO_2 through Polaris membranes, if 90% of the CO_2 is removed from the syngas, an even greater percentage of H_2S will be removed at no additional cost.



Figure 13. Mixed-gas H₂S/CO₂ selectivity in Polaris membrane modules as a function of time during the R06 test period from July 11 (Day 0) to August 20, 2011 (Day 40). The feed gas contained 320 ppm H₂S at a temperature of around 32°C. Other operating conditions and the typical feed gas composition are shown in Table 1.

Small Pilot Membrane System Demonstrating CO₂ Liquefaction

Based on the successful bench-scale module testing, a larger pilot membrane demonstration system for treating 500 lb/h of syngas was designed, built, and installed at NCCC. This system tested not only the membrane components, but the overall membrane process for syngas purification and CO_2 liquefaction. Table 3 summarizes activities conducted at NCCC using the small pilot membrane demonstration system.

Table 3.Descriptions of Three Performance Tests Run Using an MTR Small Pilot Demonstration
System Treating 500 lb/h of NCCC Syngas and Producing Liquefied CO2 from
December 2012 through December 2013.

Campaign Designation, Test Time and Dates	Feed Flow Rate (lb/hr)	Membrane Selections Tested and Changes in CO ₂ Liquefaction System
R09 12/3/2012-12/19/2012	500	System brought on line in November 2012 and successfully produced ~15 lb/hr of liquid CO_2 at 30 bar.
R10 03/21/2013-04/20/2013	500	Polaris membrane stability test. Liquid CO ₂ successfully produced.
R11 08/06/2013-09/02/2013	500	Improved Polaris membrane modules installed for testing. Liquid CO ₂ production increased to 35-40 lb/hr.

Before entering the pilot membrane system, the syngas was treated to remove sulfur compounds and tars; typical stream conditions were given in Table 1. The removal of tars (mainly heavy hydrocarbons) is critical to avoid liquid condensation and fouling in the membrane system.

The liquefaction of CO_2 is a critical step for CO_2 capture from syngas using membrane technology [5, 40]. For sequestration, the CO_2 needs to be pressurized to 150 bar for injection underground. A low energy approach is to liquefy the CO_2 at lower pressure and then pump the liquid to injection pressure [5, 40].

A simplified process flow diagram of the pilot membrane system was shown in Figure 7. During the NCCC R10 gasifier campaign (between March 21 and April 20, 2013), the first-stage membrane enriched CO₂ from 9% to 33% in the permeate. The small pilot membrane system successfully produced a liquid CO₂ stream in the condenser at -30°C and 30 bar, containing 95+% CO₂, starting from the coal-derived syngas feed containing ~9% CO₂. Figure 14(a) shows the CO₂ content in the liquid CO₂ stream as a function of time. The fluctuation in the CO₂ content (particularly to less than 80%) is presumably due to sporadic brief shutdowns of the chiller that caused the CO₂-lean gas to flow into the liquid CO₂ stream. Figure 14(b) shows the production of liquid CO₂ in the sight glass of the condenser. The liquid CO₂ production rate was 10-15 lb/hr, which corresponds to about 30-45% of the feed CO₂. These results are close to the values expected from process simulations, based on measured membrane properties.

Table 4 records several samples of measured liquid CO_2 stream compositions after the system was running at steady state for several hours, and compares these results with the simulated compositions from a commercial ChemCad 6.3 process simulator. The liquid streams were at -30°C and 30 bar. In the simulation, the H₂S content in the feed gas entering the condenser was assumed to be 5 ppmv, and the Soave-Redlich-Kwong thermodynamic equation of state was used to describe the phase behavior of the gas mixtures. As shown in Table 4, the measured compositions are fairly close to the simulated one.

(b) Liquid CO₂ in the sight glass





- Figure 14. (a) CO_2 content in the raw syngas and the liquid CO_2 stream leaving the condenser during the NCCC R10 gasifier campaign; (b) a photo of liquid CO_2 visible in the condenser sight glass. The lines in Figure 14(a) are to guide the eye. Dotted line in the photo is at the top of the CO_2 liquid accumulation.
- Table 4.Comparison of Measured Liquid CO_2 Stream Compositions and the ChemCad
Simulated Composition. The liquid streams were at -30°C and 30 bar.

Component	Measured Co	Simulated Composition		
	Stream 1	Stream 2	Stream 3	(mol%)
CO ₂	94.36	97.43	99.00	98.52
N ₂	3.67	1.34	0.32	1.26
CO	0.54	0.20	0.04	0.18
CH ₄	0.09	0.06	0.01	0.03
H ₂	0.56	0.19	0.01	0.01
H ₂ S	0.78	0.78	0.62	0.20

Following the testing described above, minor modifications were made to the small pilot demonstration system, including the addition of improved Polaris membrane modules. The system was then operated during the NCCC R11 gasifier campaign (between August 6 and September 2, 2013). The first-stage membrane enriched CO₂ from 11.5% in the feed to 40% in the permeate, which was higher than the permeate CO₂ content in the R10 gasifier campaign (about 33%), due to the better Polaris membrane modules. The membrane system continuously produced a liquid CO₂ stream in the condenser containing 95+% CO₂ at -33°C and 27 bar. The liquid CO₂ production rate improved significantly in R11 to 35-40 lb/hr, which corresponds to about 60-70% of the feed CO₂. The run time of the pilot demonstration skid was over 400 hours

during R11 with no degradation in membrane performance. Figure 15 shows the CO_2 content in the liquid CO_2 stream as a function of time.



Figure 15. CO₂ content in the raw syngas and the liquid CO₂ stream leaving the condenser during the NCCC R11 gasifier campaign.

The operation of the 500 lb/hr syngas small pilot demonstration unit shows that an integrated Polaris membrane-refrigeration system can reliably produce liquid CO_2 from coal-derived syngas. Over the course of three different syngas campaigns, the small pilot demonstration was operated on syngas for 800 hours. The successful operation of this system provides a baseline for future optimization and improvement.

CONCLUSIONS

This report describes the development of CO_2 -selective Polaris membranes for CO_2 capture from syngas, which can be divided into three phases: laboratory testing of membrane stamps, bench-scale testing of small membrane modules at a syngas production plant, and operation of commercial-sized modules on a small pilot demonstration system that produced liquid CO_2 from raw syngas. The results from this work are summarized below.

1. Laboratory testing of membrane stamps (with a membrane area of 30 cm²) provided a database of CO_2/H_2 separation properties for Polaris membranes at various temperatures, pressures, and gas compositions. The membranes showed mixed gas CO_2/H_2 selectivity above 10 at temperatures below 0°C, and pressures as high as 56 bar.

- 2. Bench-scale Polaris membrane modules were tested with coal-derived syngas at the NCCC. These semi-commercial modules (containing $1 4 \text{ m}^2$ membrane area) showed CO₂/H₂ separation properties similar to those obtained in membrane stamp tests. The test also demonstrated the long-term stability of the Polaris modules in a real syngas environment containing up to 320 ppm of H₂S. Over the course of eight different syngas campaigns from 2009 to 2013, the bench-scale system was operated on syngas for 4,400 hours.
- 3. The membrane small pilot demonstration system processed 500 lb/hr syngas (equivalent to the syngas production of a 0.15 MW_e IGCC power plant) containing ~10% CO₂, and produced a liquid CO₂ stream containing 95+% CO₂. Commercial-scale membrane modules (containing 20 m² of membrane area) were used in these tests. Over the course of three different syngas campaigns in 2012 and 2013, the pilot demonstration was operated on syngas for 800 hours capturing up to 40 lb CO₂/h (70% of feed).

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