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DEVELOPMENT OF CARBON MOLECULAR SIEVES HOLLOW FIBER MEMBRANES BASED ON POLYBENZIMIDAZOLE DOPED WITH POLYPROTIC ACIDS WITH SUPERIOR H_2/CO_2 SEPARATION PROPERTIES

Final Report
Project Period: 10/1/2018 – 1/31/2022

by

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1. EXECUTIVE SUMMARY

The goal of this project was to develop a highly efficient membrane-based process to capture CO_2 from coal-derived syngas with 95% CO_2 purity, achieving the cost of electricity (COE) 30% below the baseline capture approaches (i.e., Selexol process) when coupled with the advancement in other areas of the power generation facility. Our core approach is based on high-permeance hollow fiber membranes (HFMs) with superior H_2/CO_2 separation properties at the syngas process conditions, which can then be further utilized to design membrane reactors for process intensification of H_2 production and purification and CO_2 capture. Three organizations with complementary skills collaborated to achieve the goal, including the University at Buffalo (UB), Los Alamos National Laboratory (LANL), and Trimeric Corporation (Trimeric).

We formulated logical steps to bring the membrane technology from Technology Readiness Level (TRL) 3 (Experimental proof of concept) to TRL 4 (Laboratory scale validation in relevant environment). During the budget period (BP) 1, we screened various polymeric materials and identified polybenzimidazole doped with inorganic polyprotic acids as the desirable platform. The acid doping increases the H_2/CO_2 selectivity, and the sequential carbonization increases H_2 permeability while retaining the high selectivity. By manipulating the acid type and doping level and the carbonization temperature, we demonstrated advanced carbon molecular sieving (CMS) materials with H_2 permeability of above 200 Barrer (1 Barrer = 10^{-10} cm^3(STP) cm cm^{-2} s^{-2} $cmHg^{-1}$) and H_2/CO_2 selectivity of above 40 at 200-300°C with simulated syngas containing CO and water vapor. For example, the PBI-$(H_3PO_4)_{0.11}$ carbonized at 700 °C exhibits H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 60 at 200 °C, and H_2 permeability of 240 Barrer and H_2/CO_2 selectivity of 54 at 225 °C, which meets the targeted properties and surpasses Robeson's upper bound.

During the BP2, we focused on the conversion of the advanced CMS materials to stable HFMs. Membranes with H_2 permeance of 1,090 GPU (1 GPU = 10^{-6} cm^3(STP) cm^{-2} s^{-2} $cmHg^{-1}$) and H_2/CO_2 selectivity of 57 at 300 °C were successfully fabricated. The effects of temperature, gas compositions, pressure, and time on the separation properties were systematically investigated. Pencil modules were continuously evaluated for 219 h (dry pure gas) and 669 h (dry simulated syngas) and showed initial decline in permeance and increased H_2/CO_2 selectivity over time, ultimately achieving a steady state stable value, indicating that the ageing phenomena in the nanoporous structures of the membranes during the test.

Membrane reactors were fabricated based on the CMS membranes and evaluated for water-gas shift (WGS) reaction. The use of membranes slightly improves the conversion of the CO. However, parametric tests of the membrane reactors at various temperatures and flow rates need to be conducted, as well as the membranes with improved separation performance.

We performed a sensitivity analysis on the impact of H_2/CO_2 selectivity on the COE based on a hybrid process of a membrane unit and cryogenic unit developed by Membrane Technology and Research, Inc. (MTR). Three H_2/CO_2 selectivity (40, 60, and 15) cases were developed and compared with the baseline capture process (Case B5B) provided by the DOE report. Increasing the membrane H_2/CO_2 selectivity reduces COE, but the rate of the decrease of COE also diminishes. The COE values for H_2/CO_2 selectivities of 40 and 60 were nearly the same. As the

H_2/CO_2 selectivity increases, the inert recycling decreases, leading to smaller equipment, less auxiliary power requirements, and less heating, cooling, and refrigeration duty. The refrigeration system used to liquefy the CO_2 is the most expensive piece of equipment and consumes the most electricity within the CO_2 capture process. Increasing the CO_2 concentration in the recycle stream would improve the economics of the process by reducing the refrigeration duty requirement of the unit and also allow for higher liquefaction temperatures.

The high H_2-selective membrane developed by our team may be applicable in other separation processes where lower pressure H_2 retains value. Typically, hydrogen retains its pressure when it is separated from syngas components. Residual components may be used as low-quality fuel and then vented to the atmosphere. Applications might include control of H_2/CO ratios or mitigation of the water gas shift reaction by CO_2 recycling to the feed of a gasifier or steam methane reformer.

To summarize, we have developed industrial HFMs with the best H_2/CO_2 separation performance reported in the literature. The membranes demonstrate stability with simulated syngas and show great potential for membrane reactors for WGS reactions, lowering the cost of blue H_2 production.

2. INTRODUCTION AND OUR APPROACH

2.1. Introduction

Pre-combustion CO_2 capture for utilization and sequestration is a critical path to mitigate the CO_2 emissions to the atmosphere. In this process, coal is gasified to produce syngas, *i.e.*, H_2 and CO. The CO is converted to CO_2 by the WGS reaction, producing ~55% H_2 and ~40% CO_2 at 200-300 °C and 20-40 bar.[1] Purified H_2 can be used as a clean fuel for a combustion turbine in what is called an Integrated Gasification Combined Cycle (IGCC) process. CO_2 must be removed from the syngas stream economically to be utilized or sequestered with a modest increase in energy costs. Because the CO_2 in the syngas is relatively concentrated and at high pressure, pre-combustion CO_2 capture in the IGCC approach is easier than the CO_2 capture from post-combustion flue gas, which is at atmospheric pressure and contains only 13% CO_2.[2-5] When costs of carbon capture are included, power production by IGCC is claimed to be less costly than production by direct combustion of coal.[2]

The current leading technologies for pre-combustion CO_2 capture are physical absorption processes, such as Selexol® or Rectisol®.[6, 7] These processes are complex and consume large amounts of energy in the desorption operation. The CO_2 from the desorption unit is at low pressures, and it must be recompressed for sequestration or utilization, which is energy-intensive. The U.S. DOE has examined the economics of Selexol for CO_2 capture from coal-derived syngas produced using GEE Radiant gasifier technology. The CO_2 capture (without consideration of CO_2 transportation and storage) increases the COE from $102.6/MWh to $135.4/MWh. The goal of the DOE Carbon Capture Program is to achieve the COE 30% below the baseline approach, which is $94.8/MWh, even lower than the no capture case. Clearly, this ambitious goal can only be met with holistic development of every step in the IGCC process trains, including the CO_2 capture, compression, combustion turbines, hydrogen turbines, etc. The proposed work is expected to maximize the efficiency of the technology for CO_2 separation, making progress towards meeting the overall fossil energy performance goals of CO_2 capture.

Membrane processes have been investigated to lower the cost and energy intensity of IGCC syngas cleanup.[8-10] Because of the perceived desirability of operating at high temperatures,[11-14] much of this effort has focused on inorganic membranes, such as palladium alloys[15-20], ceramics,[21, 22] metal-organic frameworks (MOFs),[23] and graphene oxide.[24-26] While exhibiting excellent H_2/CO_2 separation properties, they are faced with challenges in the cost and reliability, scale-up of membrane production, and module fabrication. No commercial inorganic membrane system for industrial gas separations has yet been installed or is in sight.

Polymer-based membranes are much easier to implement than inorganic membranes, provided that the membrane materials demonstrate suitable separation properties.[27, 28] Production scale-up and module fabrication using polymeric membranes have been widely practiced, creating substantial engineering know-how across the polymer membrane industry.[27, 29] The goal of this project was to develop scalable membranes by engineering polymers to achieve superior H_2/CO_2 separation properties.

2.2. Current Membrane Technology

MTR had developed various process designs based on membranes for H_2 purification and CO_2 capture from coal-derived syngas. Fig. 1 shows an exemplar membrane design using an H_2-permeable, CO_2-rejecting membrane for H_2 production and a cryogenic unit for the production of liquid CO_2.[2, 30] Similar processes have also been considered by LANL and SRI International.[31, 32]

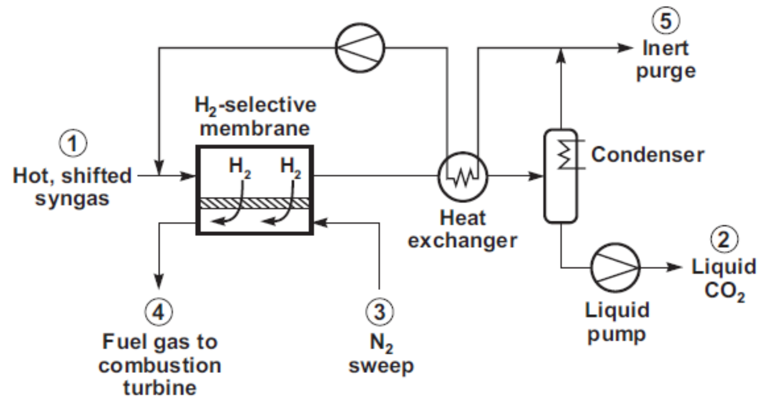

Fig. 1. A possible membrane design (proposed by MTR) integrating an H_2-selective membrane and cryogenic processes to achieve low cost and higher energy efficiency for CO_2 capture from coal-derived syngas. Figure adapted from [2, 30].

As shown in Fig. 1, the use of N_2 sweep with the H_2 separation unit based on an H_2-selective membrane partition the feed gas into a moderate-pressure H_2-rich gas and a high-pressure CO_2-rich retentate.[2, 33] The H_2-rich gas can be directly used in a turbine to generate power. The dilution with N_2 in the membrane modules increases the H_2 partial pressure difference across the membrane (or driving force), and thus it reduces the membrane area required. Also, the N_2 diluent prevents overheating and reduces NOx formation and is often required for H_2 before entering the turbine. The CO_2-rich retentate is sent to the CO_2 liquefaction/auto-refrigeration unit to achieve >95% purity. The liquefaction off-gas is either vented to remove the inert gas from the system or recycled to the CO_2-selective membrane for CO_2 recovery. The liquid CO_2 product stream can be easily pumped to the injection pressure required for enhanced oil recovery (EOR) or sequestration. The key limitation of the practice of the process shown in Figure 1 is a lack of high-performance H_2-selective, CO_2-rejecting membranes at the processing temperatures.

2.3. Our Approach and Rationale for Developing CMS HFMs

Our approach to overcoming the inherent roadblocks to simultaneously attaining high permeability and selectivity in polymers consists of starting with strongly size-sieving polymers (i.e., polybenzimidazole or PBI doped with polyprotic acids) and carbonizing them to increase both permeability and selectivity into a range suitable for commercial deployment. As shown in Fig. 2, the PBI can be doped with polyprotic acids, yielding the strongest size-sieving ability and highest H_2/CO_2 selectivity among polymers known,[34] and the following carbonization creates microcavities to increase gas permeability and ultra-microporous necks to increase size-sieving ability. The rationale is discussed below.

Increasing the H_3PO_4 doping level in PBI (defined as the molar ratio of H_3PO_4 to the PBI repeating units) decreases the pure-gas permeability and drastically increases the H_2/CO_2 selectivity at 150 °C.[34] For example, PBI shows H_2/CO_2 selectivity of 16, while PBI-$(H_3PO_4)_{1.0}$ exhibits a remarkable selectivity of 140, which is much higher than that of any previously studied polymers. H_3PO_4 can strongly interact with multi-PBI chains via proton transfer from the acid to imidazole rings of PBI and hydrogen bonding, and thus it cross-links the PBI.[35] These acid-doped PBI are significantly above the 2008 upper bound for 35 °C or 150 °C.[36] However, in general, the acid doping decreases gas permeability, increasing the costs of membrane systems.

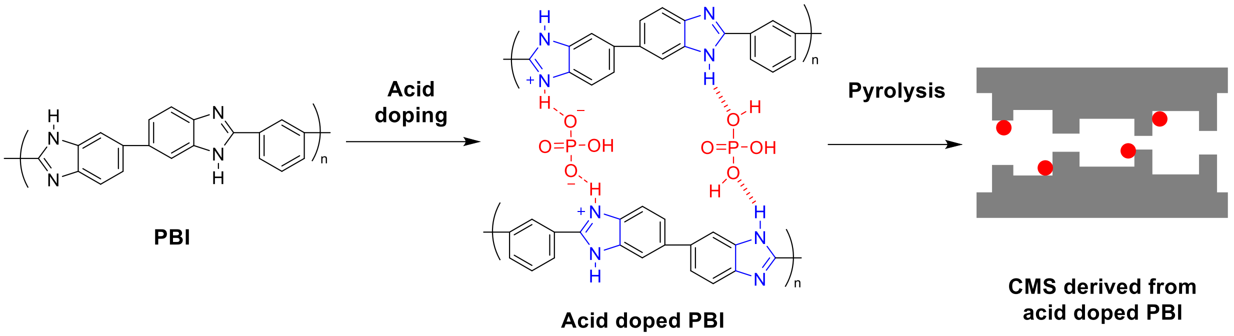

Fig. 2. Proposed CMS hollow fiber membranes derived from PBI doped with polyprotic acids in two steps. (1) Doping PBI with polyprotic acids (i.e., H_3PO_4) to increase the size-sieving ability and (2) pyrolysis of PBI/H_3PO_4 to create microcavities to increase gas permeability and ultra-microporous necks to increase molecular size-sieving ability.[37-40]

Carbon molecular sieving (CMS) membranes have attracted significant interest for gas separation because of their synergistic advantages over organic and inorganic membranes. CMS membranes contain microcavities and ultra-microporous necks, which can be tuned to simultaneously achieve high permeability and selectivity unattainable from polymers, and they have excellent thermal resistance and chemical stability in harsh environments.[41-46] We have prepared CMS membranes using PBI under the purge of ultrahigh purity N_2. The pyrolysis increases the porosity and generates a graphite-like structure (as confirmed by the Wide-Angle X-ray Diffraction patterns). As shown in Fig. 3, the carbonization of PBI dramatically increases H_2 permeability while retaining or slightly increasing H_2/CO_2 selectivity at 100 °C. All CMS samples exhibit H_2/CO_2 separation properties above the upper bound. For example, pure PBI exhibit an H_2 permeability of 12 Barrer and H_2/CO_2 selectivity of 14 at 100 °C, while the CMS prepared by pyrolysis of PBI at 800 °C shows an H_2 permeability of 670 Barrer (which is 50 times higher than pure PBI) and H_2/CO_2 selectivity of 18 at 100 °C.

We hypothesized that the CMS membranes could meet the targeted separation properties (H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40) if the starting polymers are PBI doped with polyprotic acids with strong size-sieving ability. For example, PBI-(H_3PO_4)$_{0.25}$ exhibits an H_2 permeability of 8.6 Barrer and H_2/CO_2 selectivity of 48 at 150 °C. ***The pyrolysis at 600 °C increases the permeability to 100 Barrer while retaining H_2/CO_2 selectivity at 40 at 100 °C, as shown in Fig. 3.*** During the pyrolysis, the H_3PO_4 gradually decomposes to polyphosphoric acid,[47] retaining the rigid chains and strong molecular size-sieving ability. By optimization of the acid type,

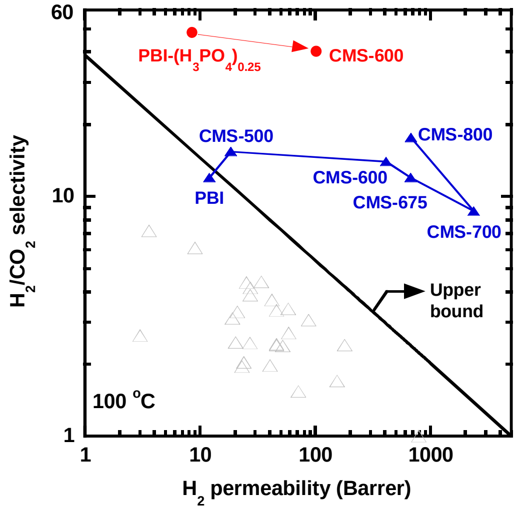

Fig. 3. Effect of pyrolysis temperatures on H_2/CO_2 separation properties in the PBI-derived CMS films at 100 °C.

composition, and pyrolysis temperature, the CMS can achieve H_2 permeability of 200 Barrer with H_2/CO_2 selectivity of 40, which can be used to prepare hollow fiber membranes with a selective layer thickness of 0.2 µm exhibiting H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40. This is feasible because carbonization has been demonstrated to increase H_2 permeability by 50 times, and LANL has successfully fabricated nearly defect-free PBI hollow fiber membranes with 0.2 µm selective layer.

3. PROJECT MANAGEMENT AND PLANNING

Our approach to developing high-performance membranes started with designing and optimizing CMS materials with superior intrinsic H_2/CO_2 separation properties, followed by fabrication and optimization of hollow fiber membranes based on the most promising CMS materials. Specifically, the proposed CMS hollow fiber membranes were prepared by doping PBI-based hollow fiber membranes with polyprotic acids, followed by pyrolysis. Both doping and pyrolysis were optimized separately with a goal of simplicity and high performance in the CMS hollow fiber membranes. Table 1 summarizes the milestones designed to evaluate the progress of the project. We had fully met the milestones and targets, and the timelines are also shown in Table 1. The detailed technical achievements are shown below.

Table 1. Overview of project milestone status.

Milestone Title/Description	Planned Completion Date	Actual Completion Date	Verification Method
Project Management Plan	10/30/2018	10/30/2018	PMP file
Project Kick-off Meeting	11/30/2018	11/30/2018	Presentation
Final Techno-Economic Analysis	9/30/2021	1/31/2022	Report
State Point Data Table	9/30/2021	1/31/2022	Report
Technology Maturation Plan	9/30/2021	1/31/2022	Report
Environmental Health and Safety Risk Assessment	9/30/2021	1/31/2022	Report
CMS films with an H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 40	12/31/2019	12/31/2019	Separation property data
Hollow fiber membranes based on PBI doped with polyprotic acids exhibiting H_2/CO_2 selectivity of 40	3/31/2020	3/31/2020	Separation property data
CMS hollow fiber membranes with H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40	9/30/2021	9/30/2021	Membranes and report
Database of H_2/CO_2 separation properties in the CMS hollow fiber membranes at various pressures, temperatures, and feed gas compositions	9/30/2021	9/30/2021	Data and report
Performance data of membrane reactors for the WGS reaction	9/30/2021	9/30/2021	Data and report

4. DEVELOPMENT OF MEMBRANE MATERIALS

4.1. PBI doped with polyprotic acids

During this BP period, we evaluated the PBI doped with several polyprotic acids with different amounts of acid groups, including 1,2-benzenedicarboxylic acid (phthalic acid or PhA), 1,3,5-benzenetricarboxylic acid (trimesic acid or TA), and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid or PyA). Fig. 4a presents the H_2/CO_2 separation performance of five organic polyprotic acid-doped PBIs at varying temperatures in Robeson's upper bound plot. All acid-doped PBIs exhibit H_2/CO_2 separation performance near or above the upper bound at 35 °C and 70 °C. Especially, PBI-$PyA_{0.16}$ ($x = 0.16$) shows a superior H_2/CO_2 selectivity of 52 with H_2 permeability of 0.9 Barrer at 35 °C. PBI-$PhA_{0.47}$ exhibits impressive H_2 permeability of 3.2 Barrer and H_2/CO_2 selectivity of 42 at 70 °C, which is above Robeson's upper bound. Increasing temperatures to 100 °C and 150 °C increases the H_2 permeability but decreases H_2/CO_2 selectivity, though their performance is still better than that of pure PBI.

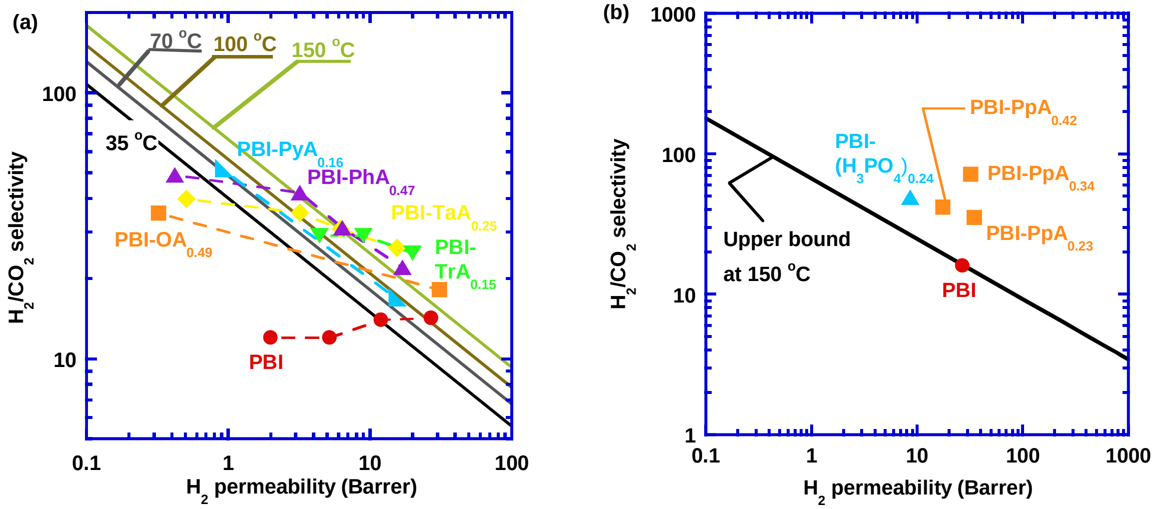

Fig. 4. (a) Comparison of organic polyprotic acid-doped PBI samples with Robeson's upper bound for H_2/CO_2 separation at varied temperatures. (b) Pure-gas permeability at 150 °C of pyrophosphoric acid-doped PBI relative to the Robeson upper bound.

Fig. 4b shows the superior H_2/CO_2 separation properties in pyrophosphoric acid (PpA)-doped PBIs. All PpA-doped PBIs exhibit better performance than phosphoric acid-doped PBI, as the PpA can transfer more hydrogen ions to PBI chains and form a more rigid structure. PBI-$(PpA)_{0.34}$ shows the best performance with H_2/CO_2 selectivity of 72 and H_2 permeability of 32 Barrer at 150 °C, breaking the permeability/selectivity tradeoff and surpassing the upper bound.

In summary, more than 8 acids with different amounts of hydrogen, PKa values, and decomposition temperatures were used to dope PBI and achieve high H_2/CO_2 separation properties. These results provide a rich database for the selection and optimization of carbonized CMS materials.

4.2. CMS membranes based on PBI/acids

Fig. 3 presents the H_3PO_4 doped PBI and its carbonized films. The molar ratio of the H_3PO_4 to the PBI repeating units (x) ranges from 0.11 to 0.28. Carbonized films with a thickness of ≈55 µm show good mechanical strength. Figure 6a shows the superior H_2/CO_2 separation properties in the carbonized PBI-$(H_3PO_4)_x$. The PBI-$(H_3PO_4)_{0.11}$ carbonized at 700 °C exhibits the H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 60 at 200 °C, which is above the upper bound. At the permeation testing temperature of 225 °C, the H_2 permeability increases to 240 Barrer, and H_2/CO_2 selectivity decreases to 54, which meets the targeted properties (H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 40).

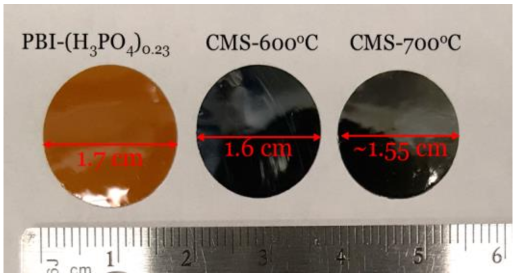

Fig. 5. Photos of PBI-$(H_3PO_4)_{0.25}$ and carbonized ones.

Fig. 6b summarizes the effect of doping level (x: defined as the molar ratio of H_3PO_4 to the PBI repeating units) on the carbonized films (at 600 °C) on the mixed-gas H_2/CO_2 separation performance at 150 °C. Increasing the doping level decreases H_2 permeance but increases H_2/CO_2 selectivity. All of the samples exhibit the separation performance above Robeson's upper bound at 150 °C.

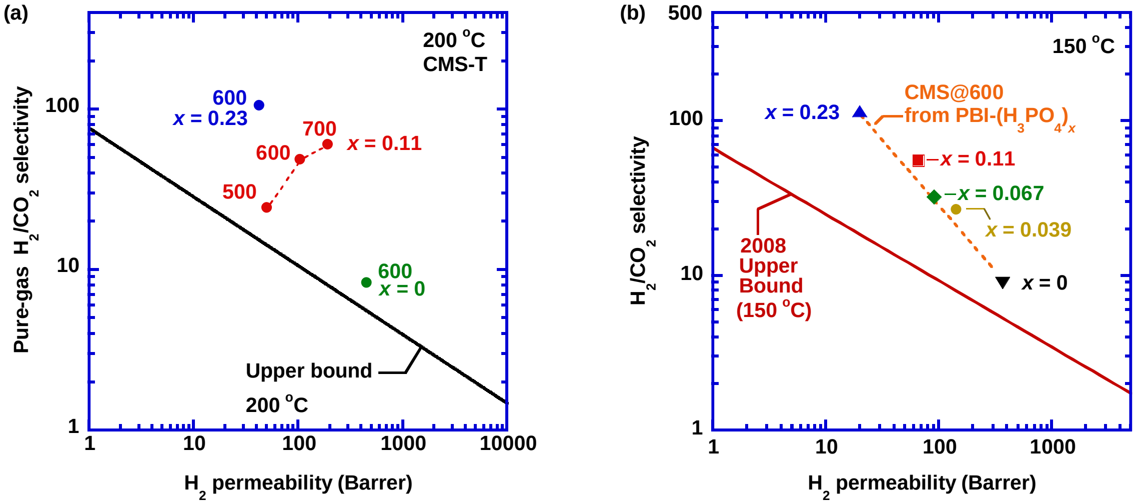

Fig. 6. (a) Pure-gas permeability at 200 °C for H_3PO_4-doped PBI CMS (x = 0 - 0.23) pyrolyzed at 500 °C-700 °C relative to the Robeson's upper bound. (b) Mixed-gas H_2/CO_2 separation properties in the carbonized PBI-$(H_3PO_4)_x$ at 150 °C

In summary, we have demonstrated that the carbonization of the acid-doped PBI significantly increases the H_2 permeability and H_2/CO_2 selectivity, and the CMS materials have met the target, i.e., H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 40.

5. DEVELOPMENT OF HOLLOW FIBER MEMBRANES

We first prepared PBI hollow fiber membranes (HFMs) and then doped them with polyprotic acids before pyrolysis. The influence of base HFM morphologies, including the porous structure of the support, dense layer thickness, and acid doping level, was evaluated on the mechanical and H_2/CO_2 separation properties of the subsequent PBI-CMS membranes.

5.1. Preparation of HFMs

Fig. 7 shows photos of the PBI and carbonized PBI hollow fiber membranes. The CMS HFMs carbonized at 650 °C show good mechanical properties.

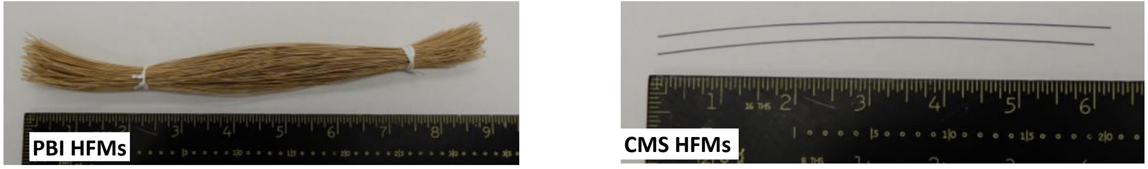

Fig. 7. PBI and CMS pyrolyzed at 650 °C hollow fiber membranes.

Fig. 8 shows the SEM photos of the doped and carbonized HFMs. As shown in Fig. 8a, the HFMs show a skin layer thickness of ~100 nm. The doping has essentially no effect on the skin and porous layers (cf. Fig. 8b), and the phosphorus element from the H_3PO_4 is evenly distributed in the skin and porous layers of the fibers. The carbonization of the doped PBI HFMs increases the skin layer thickness to ~200 nm, while most pore structures are preserved (cf. Fig. 8d). Fig. 8e shows that the P element is still distributed in the matrix.

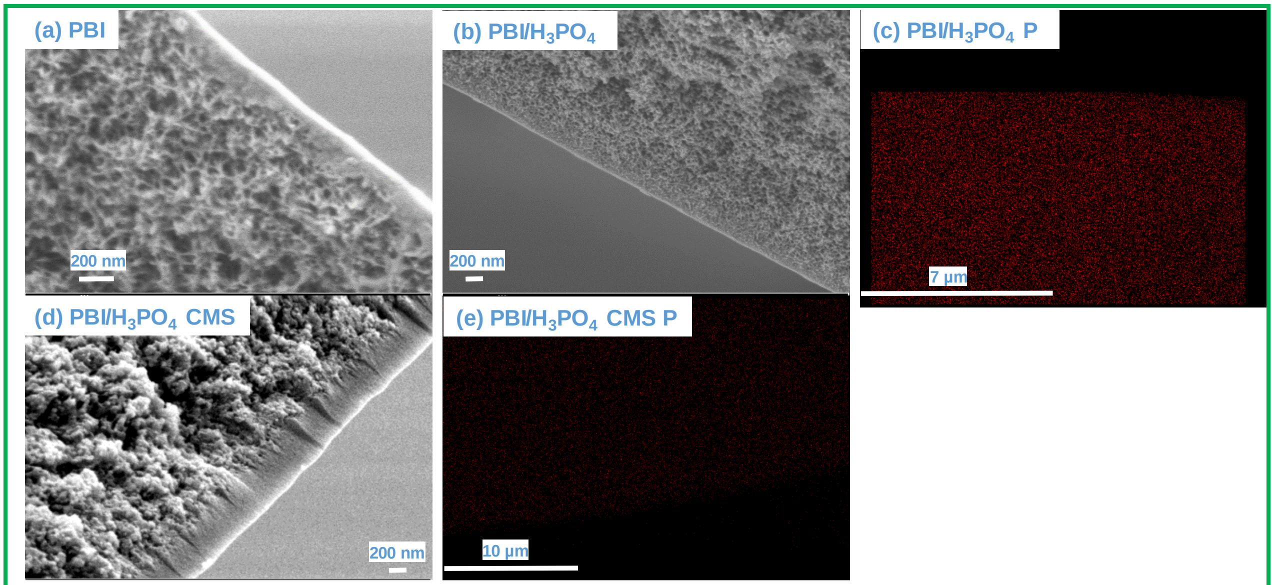

Fig. 8. SEM images of (a) PBI HFMs, (b) PBI HFMs doped by H_3PO_4, (c) P element in the HFMs, (d) PBI/H_3PO_4 carbonized at 700 °C for 2 h, and (e) P element in the PBI/H_3PO_4 CMS.

5.2. Parametric Tests of Membranes for H_2/CO_2 Separation

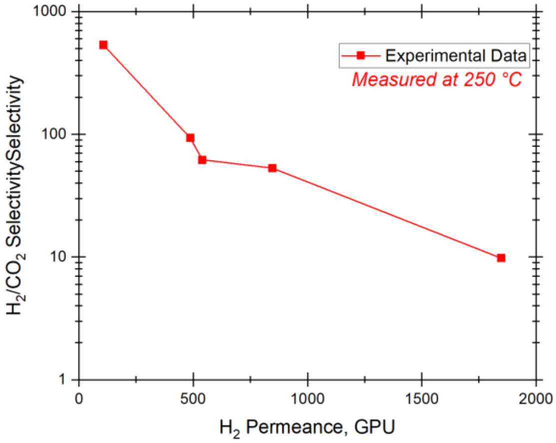

Fig. 9. Pure-gas H_2/CO_2 separation properties of a series of PBI-CMS HFMs.

During this reporting period, the PBI-CMS HFMs fabrication process was manipulated to achieve control of their H_2/CO_2 separation performance. Fig. 9 shows the H_2 permeance and H_2/CO_2 selectivity data obtained on a series of PBI-CMS HFMs fabricated under varied conditions. The H_2 permeance and H_2/CO_2 selectivity varied from 100 to 1800 GPU, while H_2/CO_2 selectivity varied from 500 to 10, respectively. Besides, symmetric ceramic-supported PPA-doped PBI-CMS HFMs were prepared, and their pure-gas H_2/CO_2 separation properties were tested at 100 °C and 100 psig. One sample showed the highest H_2/CO_2 selectivity of 170 with a H_2 permeance of 20 GPU, and another sample showed a H_2 permeance of 55 GPU with a H_2/CO_2 selectivity of 60.

Parametric evaluations of two representative PBI-CMS HFMs having combination of: 1) *high selectivity and moderate H_2 permeance (Fig. 10)*, and 2) *moderate selectivity and high permeance (Fig. 11)* were conducted. Fig. 10 shows the influence of operating conditions on the H_2/CO_2 separation performance of asymmetric PBI-CMS HFMs. The pure gas perm-selectivity was measured as a function of temperature (100 to 250 °C) and feed pressure (20 to 50 psia). The permeance is stable as a function of pressure, indicating that the membrane is free of any defects. The H_2/CO_2 selectivity increased from ca. 28 to 250 as the temperature increased from 100 to 250 °C. The increase in selectivity is primarily due to an exponential increase in the H_2 permeance as a function of temperature. This observed trend in permeance as a function of temperature is consistent with the activated diffusion transport mechanism indicating the exceptional molecular sieving characteristics of the PBI-CMS membranes.

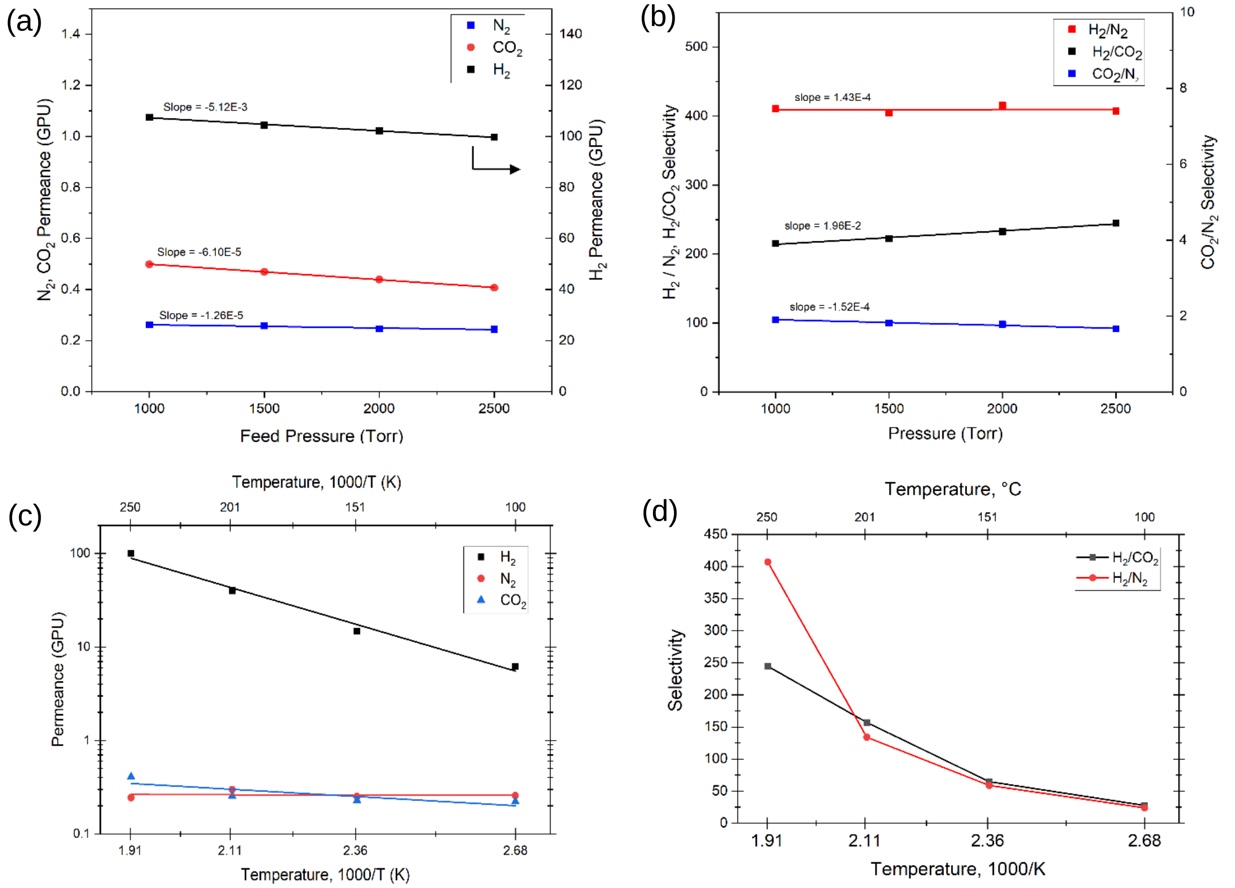

Fig. 10. Influence of feed pressure (a & b) and temperature (c & d) on ideal perm-selectivity of the PBI-CMS HFM having an asymmetric morphology.

Fig. 11 shows the influence of temperature on the H_2/CO_2 separation performance of asymmetric PBI-CMS HFMs. The ideal H_2, CO_2, and N_2 permeance increases as the temperature increases from 150 to 300 °C. The H_2/CO_2 selectivity was measured at ca. 55 for the same temperature range. ***The highest H_2 permeance of ca. 1090 GPU and H_2/CO_2 selectivity of 57 was measured at 300 °C, which exceeds the project goal of 1000 GPU and H_2/CO_2 selectivity of 40.***

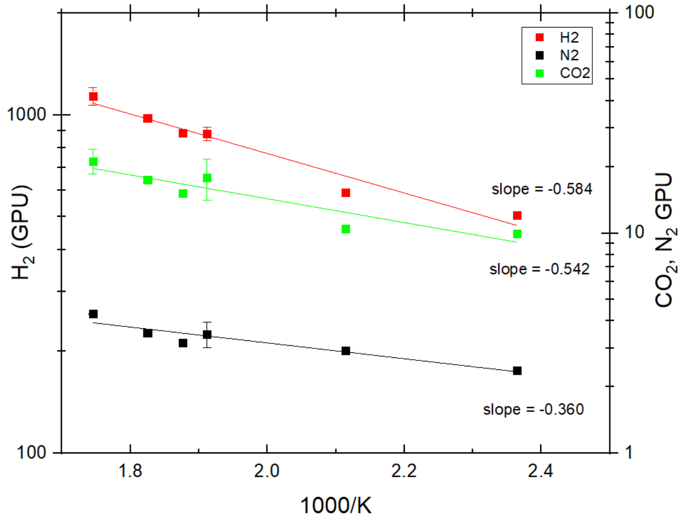

Fig. 11. Influence of operating temperature on ideal perm-selectivity of the PBI-CMS HFM.

5.3. Long-term tests

Two PBI-derived CMS HFMs (CMS#1 and CMS#2) were evaluated at syngas operating conditions. The explorations were performed in two different ways: i) long-term thermal stability of pure gas transport characteristics at 250 °C and 20 psia, and ii) long-term operational stability in simulated dry syngas fed at 250 °C and 50 psia, respectively.

The pure gas transport characteristics of CMS#1 were measured by alternating feed gases (H_2 and CO_2) every 12 h at 250 °C and 20 psia. As shown in Fig. 12a, the H_2 permeance of CMS#1 was reduced by ca. 10% from 341 GPU to 307 GPU in 220 h of continuous evaluation at 250 °C. The H_2/CO_2 selectivity of CMS#1 increased from 48 to 55 during this test period. The observed variation in the H_2 permeance and H_2/CO_2 selectivity is consistent with aging in microporous membranes.

CSM#2 was evaluated in dry simulated syngas having composition H_2:CO_2:CO:H_2S = 61.7%:37.0%:1.3%:25.3 ppm at 250 °C and 50 psia. CMS#2 maintained exceptional H_2/CO_2 selectivity over 669 h at syngas relevant process operating conditions and environments. The H_2 permeance of CMS#2 decreased from 647 to 480 GPU while H_2/CO_2 selectivity increased from 31 to 54 initially for 550 h under dry syngas feed stream. Afterward, from 550 to 669 h of evaluation, the H_2 permeance and H_2/CO_2 selectivity remained steady at 480 GPU and 54, respectively.

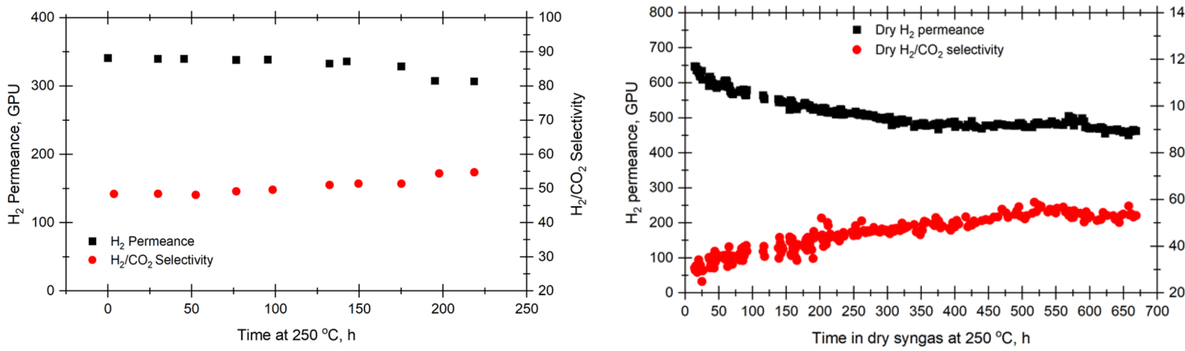

Fig. 12. (a) Change in pure gas transport characteristics of CMS#1 for 219 h by alternating feed gases (H_2 and CO_2) every 12 h at 250 °C and 20 psia. (b) Long-term operational stability of CMS#2 in simulated dry syngas fed at 250 °C and 50 psia.

6. EVALUATE CMS MEMBRANE REACTORS

UB conducted a traditional water-gas shift (WGS) reaction and membrane reactor-based WGS reaction. A membrane reactor containing a carbonized PBI hollow fiber membrane exhibiting mixed-gas H_2/CO_2 selectivity of 20 and H_2 permeance of 340 GPU at 250 °C was fabricated. The commercial low-temperature Cu/Zn/Al-based catalyst was used. The membrane reactor operates with a feed gas of 100 sccm CO/N_2 (10/90 vol%) at 100 psig and sweep gas of N_2 on the permeate side at 250 °C.

Table 2 compares the CO conversion of WGSR in a traditional fluid reactor and the membrane reactor. The use of the membrane increases the CO conversions, especially at the low loadings of the catalyst. Table 2 displays in-situ H_2/CO_2 separation performance in the membrane reactor. Increasing the catalyst loading increases both H_2 purity and recovery due to the increased H_2 partial pressure in the feed. Likewise, H_2 permeance and H_2/CO_2 selectivity increased with the catalyst loading. In conclusion, the membrane reactor increases CO conversion and improves the WGS reaction.

Table 2. CO conversion of the water-gas shift reaction (WGSR) with and without membrane reactor at 250 ºC and 100 psig.

Catalyst/SiC (g)	CO conversion (%)	
	Only catalyst	Membrane reactor
1/2.5	77	82
2/1.5	89	92
3.5/0	97	98

Table 3. Parameters of WGSR in the membrane reactor at 250 ºC and 100 psig.

Catalyst/SiC (g)	H_2 recovery (%)	H_2 purity (%)	H_2 permeance (GPU)	H_2/CO_2 selectivity
1/2.5	55	88	260	12
2/1.5	54	91	270	15
3.5/0	61	93	290	17

7. EVALUATE ECONOMIC POTENTIAL OF MEMBRANE PROCESS

Trimeric conducted a techno-economic analysis to compare the membrane process to the Case B5A (IGCC without CO_2 capture) and Case B5B (IGCC with CO_2 capture using a dual-stage Selexol unit) processes from the 2015 DOE Cost and Performance Baseline Report (Volume 1, Revision 2b).

The base case membrane developed by our team has H_2 permeance of 1,000 GPU and an H_2/CO_2 selectivity of 40 at 240°C, which represents an improvement in high-temperature H_2-selective membrane performance for CO_2 capture from IGCC syngas relative to a previous DOE report from Worley Parsons. The previous DOE report achieved H_2 permeance of 300 GPU and an H_2/CO_2 selectivity of 15 at 150°C. Our team developed more selective membranes that achieved an H_2/CO_2 selectivity of 60; their performance and impact on plant economics were explored in a sensitivity study contained in this report.

The base case membrane process reduced the COE, including Transportation, Storage, and Monitoring (TS&M), by 16% compared to Case B5B. The COE for the base case was 121.6

mills/kWh (including TS&M), representing an 18.5% increase in COE relative to the base IGCC generating plant without CO_2 capture and TS&M (Case B5A).

The main contributions towards COE reductions include lower auxiliary load and lower capital and operating costs for the base case membrane and liquefaction process relative to the baseline capture system Case B5B. Approximately 75% of the reduction in COE results from an increase in net power generation. The remaining cost savings are a result of reductions in the Total Plant Costs. Changes to the acid gas separation and CO_2 purification and compression steps result in a 30% reduction in Total Plant Costs for the base case membrane process compared to Case B5B. Significant changes to the CO_2 capture and processing area include:

- Acid Gas Separation: The membrane process removes sulfur from the membrane retentate gas using a selective MDEA treater. The DOE baseline Case B5B uses a Selexol unit to remove acid gases from the raw syngas. The Selexol unit produces separate CO_2 and H_2S product streams. The dual-stage Selexol unit is sized to process the entire syngas flow, whereas the MDEA unit processes only the retentate stream from the membrane. The MDEA unit supplies regeneration energy for H_2S desorption only. The Selexol process supplies regeneration energy for both CO_2 and H_2S desorption. The gas processing volume and acid gas capacity of chemical (MDEA) versus physical (Selexol) solvents result in a smaller acid gas removal process.
- CO_2 Purification and Compression: The membrane processes liquefy CO_2 at the syngas feed pressure and pumps the liquefied CO_2 up to pipeline pressure, as compared to the Selexol unit, which produces CO_2 at low pressure and is then compressed and dehydrated. Though refrigeration used for liquefaction represents a large auxiliary load, the power savings from pumping liquid CO_2 rather than compressing gaseous CO_2 result in lower total operating costs. Total operating costs for the membrane process are 7% lower relative to Case B5B.

Trimeric performed a sensitivity analysis on the impact of H_2/CO_2 selectivity on COE. Three H_2/CO_2 selectivity (40, 60, and 15) cases were developed. Key performance and economic metrics are summarized in Table 4 below. The baseline capture process Case B5B is included for comparison. The sensitivity study results show that increasing the membrane H_2/CO_2 selectivity reduces COE, but the rate of the decrease of COE also diminishes. COE for H_2/CO_2 selectivities of 40 and 60 was nearly the same. As the H_2/CO_2 selectivity increases, the inert recycling decreases, leading to smaller equipment, less auxiliary power requirements, and less heating, cooling, and refrigeration duty. The refrigeration system used to liquefy the CO_2 is the most expensive piece of equipment and consumes the most electricity within the CO_2 capture process. Increasing the CO_2 concentration in the recycle stream would improve the economics of the process by reducing the refrigeration duty requirement of the unit and also allow for higher liquefaction temperatures.

The high H_2-selective membrane developed by UB may be applicable in other separation processes where lower pressure H_2 retains value. Typically, hydrogen retains its pressure when it is separated from syngas components. Residual components may be used as low-quality fuel and then vented to the atmosphere. Applications might include control of H_2/CO ratios or mitigation of the water gas shift reaction by CO_2 recycling to the feed of a gasifier or steam methane reformer. More details on the TEA studies can be referred to in the TEA Report.

Table 4: Performance and Economic Summary for H_2/CO_2 Selectivity Sensitivity (Cost Basis: June 2011 USD).

	Case 1 (Base Case)	**Case 2**	**Case 3**	**Case B5B**
Process Parameters				
CO_2 Capture Technology	Membrane	Membrane	Membrane	Dual-Stage Selexol
CO_2 Processing Technology	Liquefaction / Distillation	Liquefaction / Distillation	Liquefaction / Distillation	Compression / Dehydration
Sulfur Removal Technology	MDEA / Claus	MDEA / Claus	MDEA / Claus	Dual-Stage Selexol / Claus
Membrane Parameters				
H_2 Permeance (GPU)	1,000	1,000	1,000	N/A
H_2/CO_2 Selectivity	40	60	15	N/A
Membrane Area (m^2)	15,184	23,677	8,000	N/A
CO_2 Product				
CO_2 Capture (%)	90.0	90.0	90.0	90.2
CO_2 Purity (mol%)	99.5	99.5	99.5	99.5
Power Generation				
Gross Power (kWh)	788,982	788,679	789,007	735,000
Auxiliary Load (kWh)	170,722	170,022	181,452	191,000
Net Power (kWh)	618,260	618,657	607,555	544,000
Economic Results				
Total Plant Costs ($MM)	1,726	1,723	1,959	1,840
Total Overnight Costs ($MM)	2,129	2,126	2,410	2,279
Total Annual Fixed Operating Costs ($MM)	67	67	72	69
Total Annual Variable Operating Costs ($MM)	160	160	165	164
COE (excluding TS&M) ($/MWh)	113.5	113.3	125.9	135.5
TS&M ($/MWh)	8.09	8.08	8.23	9.2
COE (Including TS&M) ($/MWh)	121.6	121.4	134.1	144.7
% Reduction in COE (Including TS&M) Relative to Case B5B	16.0	16.1	7.3	--

8. PRODUCTS AND IMPACTS

At UB, two Ph.D. students (Ms. Maryam Omidar and Mr. Hien Nguyen), a postdoctoral associate (Dr. Leiqing Hu), one M.S. student (Mr. Sankhajit Pal), and one undergraduate researcher (Vinh Bu) have been working on this project. These researchers receive interdisciplinary training on materials science, membrane separation, and CO_2 capture. Maryam and Hien graduated with a PhD, Sankhajit graduated with an MS, and Vinh had decided to pursue PhD in our lab. At LANL, the project partially supported two postdoctoral research associates and one post-MS student. They all received training in membrane fabrication and evaluation. The post-MS student was converted to full time Research Technologist at the conclusion of his two year post-MS position.

The project leads to six peer-reviewed articles and a few more in preparation. The accepted versions of the published articles have been uploaded to the DOE website. The details are shown below.

1. M. Omidvar, H. Nguyen, L. Huang, C.M. Doherty, A.J. Hill, C.M. Stafford, X. Feng, M.T. Swihart, and H. Lin, Unexpectedly Strong Size-Sieving Ability in Carbonized Polybenzimidazole for Membrane H_2/CO_2 Separation, *ACS Applied Materials and Interfaces*, 11 (50), 47365-47372 (2019)
2. L. Hu, S. Pal, H. Nguyen, V. Bui, and H. Lin, Molecularly Engineering Polymeric Membranes for H_2/CO_2 Separation at 100 °C - 300 °C, *Journal of Polymer Science*, 58(18) 2467-2481 (2020)
3. L. Hu, Bui, V. T., L. Huang, R. Singh, H. Lin, Crosslinking of polybenzimidazole using polyprotic carboxylic acids for H_2/CO_2 separation, *ACS Appl. Mater. Interface*, 13(10), 12521-12530 (2021)
4. L. Hu, V. T. Bui, A. Krishnamurthy, W. Guo, S. Pal, X. Chen, G. Zhang, R. P. Singh, M. Lupion, and H. Lin. Tailoring Sub-3.3 Å Ultramicropores in Carbon Molecular Sieve Membranes for Blue Hydrogen Production, *Science Advances*, 8 (10), abl8160 (2022)
5. L. Hu, V. T. Bui, S. Fan, W. Guo, S. Pal, Y. Ding, and H. Lin. Supramolecular Assemblies of Polybenzimidazole and Aromatic Polycarboxylic Acids with Superior Mechanical and H_2/CO_2 Separation Properties, *J. Mater. Chem. A*, in press (2022)
6. L. Hu, V. T Bui, S. Pal, W. Guo, A. Subramanian, K. Kisslinger, S. Fan, C.-Y. Nam, Y. Ding, and H. Lin. In situ synergistic growth of crystalline and polymer-incorporated amorphous ZIF-8 in polybenzimidazole achieving hierarchical nanostructures for H_2/CO_2 separation, Submitted (2022)

The results from the project were also disseminated through various conferences. A few oral presentations shown below.

1. H. Lin, Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties, NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 26, 2019.
2. H. Lin, “Refining Polybenzimidazole (PBI) for Membrane H_2/CO_2 Separation,” Air Liquide, America, September 16, 2019.
3. H. Nguyen and H. Lin, Polybenzimidazole-Derived Carbon Molecular Sieves with Microcavities and Ultra-Microporous Channels Achieving Superior Membrane H_2/CO_2

Separation Properties, Materials Research Society Conference, Boston, MA, December 4, 2019.

4. L. Hu, Synergistic Thermolabile Cross-linking and Low-temperature Carbonization to Create Sub-3.3 Å Ultramicropores for Membrane H_2/CO_2 Separation, North American Membrane Society Conference, Estes Park, CO, August 2021
5. B. T. Bui, L. Hu, H. Lin, In Situ Growth of ZIF Nanoparticles to Cross-link Polybenzimidazole and Achieve Superior H_2/CO_2 Separation Performance, North American Membrane Society Conference, Estes Park, CO, August 2021
6. H. Nguyen, M. Omidvar, L. Huang, C. Doherty, A. Hill, and H. Lin, Carbon Molecular Sieves with Superior H_2/CO_2 Separation Properties at Elevated Temperatures for Pre-combustion CO_2 Capture, North American Membrane Society Meeting, virtual meeting, May 18, 2020
7. H. Lin, Molecularly engineering polymeric membranes for pre-combustion CO_2 capture at 150 °C and above, AIChE Annual Meeting, November 18, 2020.
8. L. Hu, Carbonized pyrophosphoric acid-doped PBIs for high-temperature H_2/CO_2 separation, AIChE Annual Meeting, November 19, 2020.
9. L. Hu, H. Lin, Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties, Carbon Management and Natural Gas & Oil Research Project Review Meeting, August 2021
10. L. Hu, H. Lin, In-situ growth of ZIFs in polybenzimidazole to achieve superior H_2/CO_2 separation performance, 2021 AIChE Annual Meeting, Boston, MA, November 11, 2021.
11. L. Hu, H. Lin, Facilely cross-linking polybenzimidazole with polyprotic acids to enhance H_2/CO_2 selectivity, 2021 AIChE Annual Meeting, Boston, MA, November 9, 2021.
12. R. Singh, High selectivity and Throughput carbon molecular sieve hollow fiber membranes, Air Liquide, July 2021
13. R. Singh, Polybenzimidazole membrane technology for elevated temperature hydrogen separation, National Science Foundation – Center for Innovative and Strategic Transformation of Alkane Resources (CISTAR), August 2020.

STATE-POINT DATA FOR MEMBRANE BASED SYSTEMS

	Units	Measured/ Estimated Performance	Projected Performance
Materials Properties			
Materials of Fabrication for Selective Layer		Carbonized acid-doped polybenzimidazole	
Materials of Fabrication for Support Layer (if applicable)		Polybenzimidazole (PBI)	
Nominal Thickness of Selective Layer (μm)		0.2	0.2
Membrane Geometry		Hollow fiber	Hollow fiber
Max Trans-Membrane Pressure	bar	20	50
Hours tested without significant degradation		120	500
Membrane Performance			
Temperature	°C	150	200 - 350
Pressure Normalized Flux for Permeate (H_2)	GPU	1000	1000
Permeate/H_2O Selectivity	-	0.5	0.5
Permeate/N_2 Selectivity	-	80	80
Permeate/H_2S Selectivity	-	80	80
CO_2/H_2 Selectivity	-	0.025	0.017
H_2/CO_2 Selectivity	-	40	60
Type of Measurement (Ideal or mixed gas)	-	Mixed-gas	Mixed-gas
Proposed Module Design			
Flow Arrangement	-	Counter-current	
Packing Density	m^2/m^3	~1,000	
Shell-Side Fluid	-	Retentate	

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