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Title: Fact Sheet: Polymer-Based Carbon Dioxide Capture Membrane Systems

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Project Title: **Polymer-Based Carbon Dioxide Capture Membrane Systems**		
Technology Area: Pre-Combustion Membranes	**Project Focus:** High Temperature Polymer Based Membrane	**Technology Maturity:** Pre-pilot testing, prototype development, manufacturing methodology development/optimization

Primary Project Goal:

To develop and demonstrate polymer-based membrane structures, deployment platforms, and sealing technologies that achieve the critical combination of high selectivity, high permeability, chemical stability, and mechanical stability all at elevated temperatures (>150°C) and packaged in a scalable, economically viable, high area density system amenable to incorporation into an integrated gasification combined cycle (IGCC) plant for pre-combustion carbon dioxide (CO_2) capture.

Technical Goals:

- Continue to develop and demonstrate high temperature polybenzimidazole (PBI)-based membrane chemistries and morphologies for carbon capture and hydrogen purification from coal-derived shifted syngas
    - Operation under industrially relevant process conditions
    - Stability in the presence of anticipated concentrations of primary syngas components and impurities
- Develop the fabrication materials and methods required to realize those materials and morphologies as defect-free high area density hollow fiber membranes (HFMs) and modules
- Demonstrate the technology potential via materials and membrane performance evaluation under industrially relevant process conditions
    - Conduct permselectivity and materials stability evaluations under realistic syngas conditions
    - Reduce perceived technical risks of utilizing a polymeric membrane based technology in a challenging (thermal, chemical, mechanical) syngas environment

Technical Content:

Los Alamos National Laboratory (LANL) work to-date has demonstrated that PBI and other benzimidazole-based materials show promise as membranes for pre-combustion-based capture of CO_2. The primary goals of this project are: to continue to develop and demonstrate PBI-based materials and morphologies as a separation media for hydrogen purification and carbon capture, to demonstrate the performance of those materials in industrially relevant process streams, and to further develop fabrication methodologies and separation schemes to support the technically and economically viable integration of a pre-combustion CO_2 capture system based on these materials into an advanced IGCC plant. The ultimate achievement in the area of CO_2 capture is the production of a CO_2-rich stream at pressure using methods compatible with the overall DOE NETL Carbon Capture Program research goals. The work that this project team is pursuing is aligned directly with these capture goals and utilizes a pre-combustion capture approach focused on the continued development of high-temperature polymer-based membranes that will ultimately be integrated into an advanced IGCC process.

A PBI-based membrane selective layer chemistry is being utilized by our project team. PBI is a unique polymer family that is stable to temperatures approaching 500°C. PBI possesses excellent chemical resistance, a very high glass transition temperature (~460 to 500°C), good mechanical properties, and an appropriate level of processability. The PBI-based membranes developed by this project team have demonstrated operating temperatures significantly higher than 150°C (up to 400 to 450°C) with excellent chemical, mechanical, and hydrothermal stability. The materials and membranes that have been developed and continue to be optimized as part of this project outperform any polymer-based membrane available commercially or reported in the literature for separations involving hydrogen. This achievement is validated via membrane productivity (separation factor and flux) comparisons (Figure 1). The improved performance of this technology in an application such as IGCC-integrated capture is further substantiated by the accessible operating temperature range (up to 400°C), long-term hydrothermal stability, sulfur tolerance, and overall durability of the proposed membrane materials in these challenging pre-combustion environments. These characteristics have been validated via extensive evaluations of our polymer-based membrane in simulated syngas environments containing H_2, CO_2, CH_4, N_2, CO, H_2O, and H_2S from 25 to 400°C and demonstration of the membrane's thermal stability via 300+ days in operation at 250°C. To-date these achievements and material/membrane property validations have been largely conducted on flat sheet and tubular platform membranes.

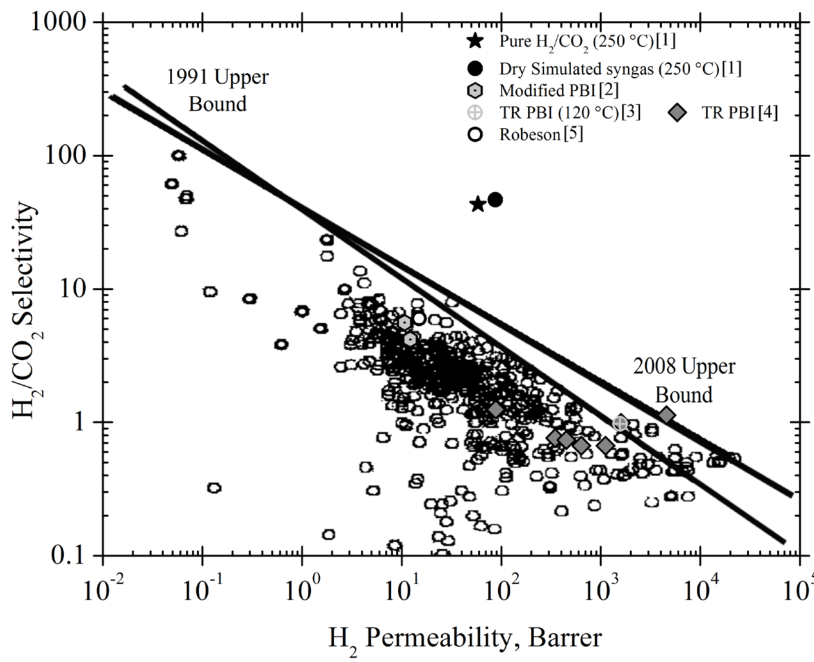

Figure 1: Robeson plot comparing the PBI composite membrane [1] with other polymeric membranes tested for the H_2/CO_2 separation. The lines represents the 1991 and 2008 upper bound from Robeson [5], the black circles (O) are the corresponding experimental data from Robeson [5]. The hexagons (⬡) represent modified PBI membranes [2] and the diamonds (◆) and cross (⊕) represent the thermally rearranged (TR) PBI-based polymer membranes [3,4]. (Data from: **[1]** Berchtold and Singh *et.al.* JMS, 415 (2012) **[2]** Kumbharkar et.al., 286 (2006) **[3]** Park et.al., 259 (2010) **[4]** Han et.al., 357 (2010) **[5]** Robeson, 320 (2008)).

A previous programmatic effort was focused on the utilization of the PBI formulations as a selective layer deposited on and supported by a unique porous metal substrate (fabricated by Pall Corporation). Systems, economic, and commercialization analyses conducted by NETL, LANL, and others, combined with in- and out-of-laboratory testing, established the technical viability of the technology and indicated the strong potential for the membrane-based capture technology to meet and exceed the DOE Carbon Capture Program goals. However, these analyses also made clear the need to cut the costs of the support material and increase the area density realized by the ultimate module design in order to realize the desired step-change in both performance and cost of CO_2 capture associated with the use of this membrane-based capture technology. One promising option for achieving a substantial increase in active membrane area density and mitigating the cost of a metal or inorganic material-based support is the use of a hollow fiber membrane (HFM) platform. A HFM is the membrane configuration with the highest achievable packing density (i.e., the highest membrane selective area density). HFM modules have been fabricated to obtain selective area densities as high as 30,000 m^2/m^3. This affords the opportunity to achieve several orders of magnitude improvement over the density achievable with the previous polymeric-metallic membrane platform (ca. 250 m^2/m^3). Realization of such a step change in area density with the materials previously developed by this team would lead to substantial economic and technical benefits.

The work being conducted as part of this continuing development and demonstration effort includes the non-trivial advancement of realizing these exceptional materials in a commercially viable, all polymeric, HFM platform (Figure 2). HFMs provide numerous opportunities for realization of the desired performance and economic enhancements associated with the use of this membrane based capture technology for pre-combustion capture. Hollow fibers represent a high area density membrane platform, which will reduce the size requirement of the costly, high-temperature-tolerant membrane module housings, will minimize membrane support costs thru their all polymeric design, and will facilitate membrane flux maximization thru processing facilitated selective layer thickness minimization. We will explore the synergies that derive from combining these advantageous hollow fiber characteristics to produce a high-flux, high area density membrane platform that meets or exceeds DOE system performance and economic goals.

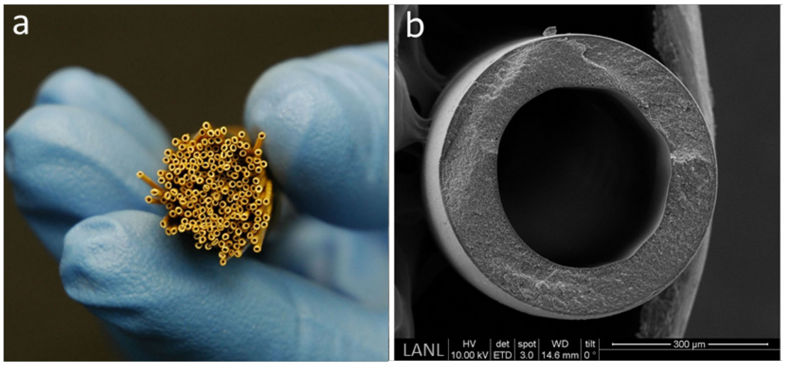

Figure 2: (a) On-end image of a small PBI hollow fiber bundle prepared at LANL. (b) SEM micrograph of PBI hollow fiber showing representative HFM prepared by LANL.

Current and future work is aimed at translation of the previously developed membrane materials chemistries into a high area density HFM platform via commercially viable hollow fiber membrane manufacturing methods, developing and deploying defect-mitigation strategies for optimizing membrane performance and durability, and demonstrating the produced membranes in simulated and ultimately real process environments with the overarching goal of technology progression towards commercialization.

Table 1: Membrane Process Parameters

	Units	Current R&D Value		Target R&D Value
Materials Properties				
Materials of Fabrication for Selective Layer		high T_g polymer		
Materials of Fabrication for Support Layer		metallic composite	high T_g polymer	high T_g polymer
Nominal Thickness of Selective Layer	μm	0.6	1.3	0.1
Membrane Geometry		tubular	hollow fiber	hollow fiber
Maximum Trans-Membrane Pressure (TMP)	bar	30*	4.5*	35
Hours Tested Without Significant Degradation		8400(@ 250°C)‡	288‡	500
Manufacturing Cost for Membrane Material	$\$/m^2$	>100		15
Membrane Performance				
Temperature	°C	250	150-350	150-350
H_2 Pressure Normalized Flux	GPU	170	40-75	250
H_2/H_2O Selectivity	-	~1		
H_2/CO_2 Selectivity	-	42	35-20	90-40
H_2/H_2S Selectivity	-	>1,800		>1,800
Sulfur Tolerance	ppm	10,000		10,000
Type of Measurement	-	mixed & pure	pure	mixed
Proposed Module Design (Preliminary)				
Flow Arrangement	-	counter	complex	
Packing Density	m^2/m^3	250		2000-15,000
Shell-Side Fluid	-	retentate		
Syngas Gas Flowrate	scf / m^2 / hr	210-240		
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	**	50 **

H_2 Recovery, Purity, and Pressure	% / % / bar	>98	‡	20 ‡
Pressure Drops Shell/Tube Side	bar	Not yet defined‡‡		
Estimated Module Cost of Manufacturing and Installation	$ / kg/hr	Not yet defined‡‡		

* Max TMP tested, **not** max achievable TMP

‡ Time to test conclusion, no degradation observed

** Gasifier, coal feedstock, and upstream unit operation (e.g., WGS) specifications dependent

‡ Tailored to match the turbine inlet specifications, e.g., 125 LHV btu/ft^3 and 20 bar permeate

‡‡ Optimized HFM geometry, module geometry, and all module design components are not fully defined

<u>Description of Membrane Permeation Mechanism:</u> Solution Diffusion where at the proposed elevated separation temperatures, permeability is dominated by gas diffusivity in the selective layer.

<u>Contaminant Resistance:</u> Excellent resistance to syngas contaminants

<u>Syngas Pretreatment Requirements:</u> Particulate removal

<u>Process Design Concept:</u> Multiple location possibilities largely influenced by gasifier type (syngas pressure and quality), the employed WGS technology, and the presence or lack thereof of a warm temperature gas clean-up for sulfur removal prior to the capture step. For performance benchmark purposes, the membrane separation is conducted post low temperature (250°C) WGS. Nitrogen from the ASU is used as a membrane sweep gas with the sweep flows specified based on the turbine inlet heating value specification. Initial evaluations have utilized GE F-class turbine specifications and GE (Texaco) gasifier – radiant operation.

<u>Proposed Module Design:</u> Hollow fiber module design comprised of high pressure, high temperature housings and components. The syngas will be processed at process T & P. The conditions of the primary separation position will be matched to those at the exit of the low temperature water gas shift reactor. The pressure drop utilized will be tailored based on the turbine inlet pressure. This process favors conditions created by gasifiers that operate at higher pressure.

Technology Advantages:

- Broad accessible membrane operating temperature range (150 to 300+ °C) facilitating increased opportunity for process integration/optimization.
- Demonstrated long-term hydrothermal stability, sulfur tolerance, and overall durability of selective layer materials.
- Membrane-based technology competitive advantages: modularity, low-maintenance operations, small footprint, low/no waste process, and flexible design opportunities.

R&D Challenges:

- Design, control, prediction, and synthesis of tailored material morphologies in hollow fiber format
- Realizing high permeance, defect-free gas separation viable hollow fibers
- Realizing sealing materials and methods compatible with the target materials' and process' thermal, chemical, and mechanical characteristics/environments.

Results To Date/Accomplishments:

- Translation to robust, high permeance, hollow fiber based module platform underway
    - Fundamental understanding of multicomponent phase inversion system developed
    - Translation of those learnings into fiber fabrication protocols established

- Control of selective layer thickness demonstrated using processing and phase inversion manipulations
- Successful demonstration of hollow fiber membranes with permselectivity characteristics matching that of the shell and tube composite membranes.
- Module fabrication materials and methods developed enabling HFM evaluation to 350 °C
  - Fiber and module integrity and performance to 350 °C demonstrated
- Demonstrated success in developing methods for defect healing and sealing
  - Performance of membrane prototypes incorporating healing and sealing approaches indicates exceptional opportunities for defect mitigation with minimal transport resistance using developed methods

Next Steps:

- Continued development and demonstration of HFM fabrication methodologies to achieve high permeance membranes in defect minimized platforms
  - Further minimization of selective layer thickness – permselectivity optimization
  - Optimization of HFM geometry
  - Further development, demonstration, and implementation of fiber healing and sealing materials and methods
  - Module demonstration in "real" coal derived IGCC syngas at the NCCC - PSDF

Available Reports/Technical Papers/Presentations:

- Polybenzimidazole composite membranes for high temperature synthesis gas separations, K.A. Berchtold, R.P. Singh, J.S. Young, K.W. Dudeck, *J. of Membrane Science* 415-416 (2012) 265.
- High-Temperature polymer-based membrane systems for pre-combustion CO_2 capture, K.A. Berchtold, *2012 NETL CO2 Capture Technology Meeting* (July 2012) http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/4-Thursday/K Berchtold-LANL-Polymer-based Membrane.pdf
- Tuning microcavities in thermally rearranged polymer membranes for CO_2 capture, Han, S. H.; Kwon, H. J.; et al, *Physical Chemistry Chemical Physics* 14(13) (2012) 4365.
- Greening coal: breakthroughs and challenges in carbon capture and storage", P. Stauffer, G. Keating, R. Middleton, H. Viswanathan, K.A. Berchtold, R.P. Singh, R. Pawar, A. Mancino, *Environmental Science & Technology*, 45 (2011) 8597.
- Simulation of a process to capture CO_2 From IGCC syngas using a high temperature PBI membrane, G.D. Krishnan, D. Steele, K.C. O'Brien, R. Callahan, K.A. Berchtold, and J.D. Figueroa, *Energy Procedia*, 1(1) (2009) 4079.
- Towards a pilot-scale membrane system for pre-combustion CO_2 separation, K.C. O'Brien, G. Krishnan, K.A. Berchtold, J.D. Figueroa, et. al. *Energy Procedia*, 1(1) (2009) 287.

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