PRE-COMBUSTION CARBON CAPTURE BY A NANOPOROUS, SUPERHYDROPHOBIC MEMBRANE CONTACTOR PROCESS

primary project goals

Gas Technologies Institute set out to develop cost-effective separation technology for carbon dioxide (CO_2) capture from synthesis gas (syngas) based on a hollow-fiber membrane contactor.

technical goals

- Design an energy-efficient, CO_2 recovery process that minimizes hydrogen loss.
- Tailor highly chemical-inert and temperature-stable, superhydrophobic, hollow-fiber poly (ether ether ketone) (PEEK) membrane for pre-combustion CO_2 capture.
- Manufacture a low-cost integrated membrane module.

technical content

The membrane contactor is a novel gas separation technology, advanced mass transfer device that operates with a liquid on one side of the membrane and gas on the other. Unlike gas separation membranes where a differential pressure across the membrane provides the driving force for separation, the membrane contactor can operate with pressures that are almost the same on both sides of the membrane. The driving force is the chemical potential of CO_2 absorption into the liquid. This process is thus easily tailored to suit the needs for pre-combustion CO_2 capture.

The hollow-fiber membrane is manufactured from an engineered material, called PEEK by PoroGen Corporation, using a patented process. Some key characteristics that make PEEK attractive for this process are: high heat resistance, high rigidity, high dimensional stability, good strength, excellent chemical resistance, excellent hydrolytic stability, an average pore size of 1 to 50 nm, an average porosity of 40 to 70 percent, and an 800-pound per square inch (psi) water breakthrough pressure.

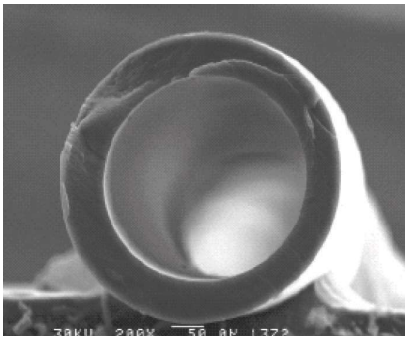

Figure 1: PEEK Hollow Fiber

The PEEK hollow-fiber membrane is nanoporous and can be surface modified to achieve superhydrophobicity; fiber OD can range from 200µm to 1mm; and fibers can be made with thin wall (<25µ) due to the strength of PEEK. The PEEK membrane pore size can be controlled from 1 to 50 nm, and asymmetric membrane structures can be utilized for high performance. The hollow fiber has a high burst pressure of greater than 500 pounds per

technology maturity:

Bench-Scale Using Simulated Syngas

project focus:

Nanoporous, Superhydrophobic Membrane Contactor Process

participant:

Gas Technology Institute

project number:

FE0000646

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Aker Process Solutions

performance period:

10/1/09 – 3/31/12

square inch gauge (psig), and a high collapse pressure of greater than 1,000 psig.

The advanced hollow-fiber module is constructed by computer-controlled helical winding. The modules exhibit favorable flow dynamics with minimal pressure drop, high uniform packing density, and thermodynamically efficient counter-current flow configuration.

The project was divided into two phases. The activities of Phase I included the development of hollow-fiber membranes suitable for the membrane contactor application with improved mass transfer, establishing feasibility of the proposed technology for syngas CO_2 separation, and performing initial process design and economic analysis based on test data.

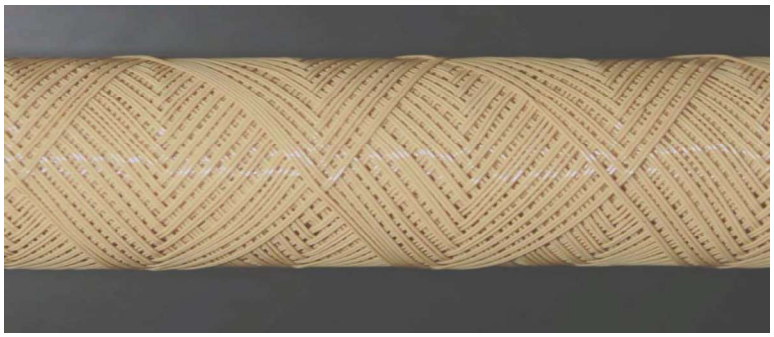

Figure 2: Advanced Hollow-Fiber Module Design

The focus of the Phase II activity was to scale-up the process from lab to bench scale. This included scale-up of the membrane module fabrication process so that membrane modules of the size suitable for large-scale application could be manufactured; bench-scale testing of the membrane contactor process stability and sensitivity to process variations; and refinement of the process economics based on bench-test data.

TABLE 1: GTI MEMBRANE PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Perfluoro-oligomer	Perfluoro-oligomer/Polymer
Materials of Fabrication for Support Layer		PEEK	PEEK
Nominal Thickness of Selective Layer	µm	100	100
Membrane Geometry		Hollow Fiber	Hollow Fiber
Maximum Trans-Membrane Pressure	bar	3.4	Maximize
Hours Tested Without Significant Degradation		120	120
Manufacturing Cost for Membrane Material	$/m^2	Proprietary	Proprietary
Membrane Performance			
Temperature	°C	0 – 50	Maximize
H_2 Pressure Normalized Flux	GPU or equivalent		
CO_2 Removal Rate	kg/m^2/h	6	1.5
H_2/H_2O Selectivity	-	3.7x10^{-6}	3.7x10^{-6}
H_2/CO_2 Selectivity	-	2.65x10^{-7}	2.65x10^{-7}
H_2/H_2S Selectivity	-	7.5x10-5	7.5x10-5
Sulfur Tolerance	ppm	>100,000	>100,000
Type of Measurement	-	Equilibrium Calculation	Gas Analysis
Proposed Module Design		-	
Flow Arrangement	-	Counter-Current	Counter-Current
Packing Density	m^2/m^3	500 – 1,000	500 – 1,000
Shell-Side Fluid	-	Water, methanol, aMDEA	Water, methanol, Selexol

TABLE 1: GTI MEMBRANE PARAMETERS

	Units	Current R&D Value	Target R&D Value
Membrane Area/Module	m^2	1	100
Syngas Gas Flowrate	L/min	12	1,200
Solvent Flowrate	L/min	1.2	120
CO_2 Recovery, Purity, and Pressure	% / % / bar	90/96/5	90/96/5
H_2 Recovery, Purity, and Pressure	% / % / bar	99/91/50	99/91/50
Pressure Drops Shell/Tube Side	bar	0.4/0.04	0.4/0.04
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	$100	$40

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Contaminant Resistance – Membrane is resistant to all contaminants. Absorbents will be affected by contaminants to a lesser extent than a conventional packed or tray column.

technology advantages

- Counter-current flow allows for the most efficient mass transfer, thermodynamically.
- Computer-controlled winding provides structured packing to enable enhanced turbulence flow at fiber surface.
- High temperature stability for the desorption step.
- High liquid breakthrough pressure (no liquid wet out), high membrane integrity.
- High membrane productivity.

R&D challenges

- Membrane hydrophobic properties change with solvent contact, causing leakage.
- Mass transfer coefficient of 1.5 kg/m^2hr used in the economic evaluation was not sufficiently high for gas absorption in the membrane contactor.

results to date/accomplishments

- Membrane contactor stability and life testing completed.
- 90 percent CO_2 removal from simulated syngas demonstrated.
- High mass transfer coefficients achieved.
- Commercial size membrane contactor designed.
- Slipstream testing completed.

next steps

- The project ended on March 31, 2012.
- Additional module design and testing required to operate with more viscous solvents.
- Scale-up testing with 8-in diameter modules with coal-derived syngas.

available reports/technical papers/presentations

Meyer, H.; Zhou, J.; Bikson, B.; and Ding, Y., "Pre-combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process," presented at the 2011 NETL CO_2 Capture Technology Meeting in Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/5-Friday/26Aug11-Meyer-GTI-Pre-Combustion%20Capture%20by%20Nanoporous%20Membr.pdf*.

Zhou, J.; Meyer, H.; and Bikson, B., "Pre-combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process," presented at the 2010 NETL CO_2 Capture Technology Meeting in Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/friday/Shaojun%20Zhou%20-%20FE0000646.pdf*.

Meyer, H.; Zhou, J.; and Leppin, D., "Advanced H_2S and CO_2 Removal Technologies for Synthesis Gases", presented at the 4th International Freiberg Conference of IGCC and XtL Technologies, Dresden, Germany, May 2010. *http://www.gasification-freiberg.org/PortalData/1/Resources/documents/paper/IFC_2010/14-2-Meyer.pdf*.

Zhou, S.J.; Meyer, H.; Bikson, B.; and Ding, Y., "Hybrid Membrane Absorption Process for Post Combustion CO_2 Capture." AIChE Spring Meeting, San Antonio, Texas, March 2010. *http://www.aiche.org/cei/resources/chemeondemand/conference-presentations/hybrid-membrane-absorption-process-post-combustion-co2-capture*.