CO_2 CAPTURE MEMBRANE PROCESS FOR POWER PLANT FLUE GAS

technology maturity:

Bench-Scale, Using Simulated Flue Gas

project focus:

Hollow-Fiber, Polymeric Membrane

participant:

Research Triangle Institute

project number:

NT0005313

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partners:

Arkema
Generon IGS

performance period:

10/1/08 – 9/30/11

primary project goals

Research Triangle Institute (RTI) set out to develop an advanced hollow-fiber, polymeric membrane-based process that can be cost-effectively retrofitted into current pulverized coal (PC)-fired power plants to capture at least 90 percent of the carbon dioxide (CO_2) from the plant's flue gas.

technical goals

- Develop new fluorinated polymers as membrane materials that have superior CO_2 separation properties compared to conventional and competitive membrane platforms. A minimum selectivity of 30 for CO_2 over nitrogen (N_2) and CO_2 permeance in excess of 300 gas permeance unit (GPU) are targeted. Fluorinated polymers are a promising material platform because they exhibit excellent chemical stability to moisture, sulfur dioxide (SO_2), and nitrogen oxide (NO_x) contaminants present in flue gas.
- Develop next-generation polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 permeance than current commercial polycarbonate membranes.
- Develop and fabricate improved membrane hollow fibers and module designs to handle large flue gas flow rates and high CO_2 permeate flow rates with minimal pressure drop.
- Identify and develop CO_2 capture membrane process design and integration strategies suitable for retrofit installation.

technical content

Project research efforts include development of membrane materials and membrane hollow fibers, membrane module design and fabrication, and process design.

RTI pursued the development of two membrane material platforms. As a near-term membrane platform solution, RTI worked with Generon to develop next-generation, high-flux polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 permeance than current-generation, commercial polycarbonate membranes. Hollow-fiber membranes made from the high-flux polycarbonate have been successfully developed, scaled up, and fabricated into module separation devices. Laboratory-scale membrane modules have been studied with simulated flue gas mixtures with and without flue gas contaminants.

For a longer-term membrane platform solution, RTI worked with Arkema to develop improved CO_2 capture membrane materials based on the polymer chemistry of polyvinylidene fluoride [PVDF], the chemical structure of which is shown in Figure 1 and comprises the [CH_2-CF2]n repeat unit. PVDF is well suited for contact with flue gas, possessing high chemical resistance to acids and oxidants, specific affinity for CO_2 for high CO_2 solubility, and high thermal stability (Td ≈ 340°C). PVDF also features excellent physical and mechanical properties, durability, and longevity suited to the fiber extrusion process used to fabricate mem-

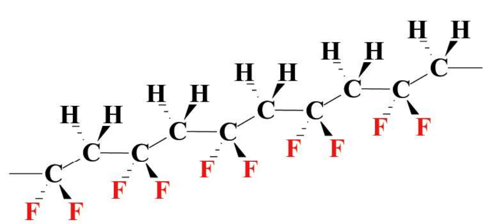

Figure 1: Chemical Structure of PVDF

brane hollow fibers. However, conventional PVDF is a homopolymer that is semicrystalline and has CO_2/N_2 selectivity of ≈23 and low CO_2 permeance of ≈10 GPU. Arkema has pursued synthesizing and developing advanced, PVDF based copolymers possessing improved CO_2 permeance and selectivity.

In this project, the membrane under development was in the form of hollow fibers that are packaged into compact, high surface area-to-volume module devices. Multiple modules were utilized in a given CO_2 capture membrane system for power plant applications due to the large quantity of flue gas to be processed. The modularity of the membrane separation devices allows for easy adaptation to different levels of CO_2 removal desired by simply adding or subtracting the number of membrane modules used. Figure 2 shows a cross-section of a hollow-fiber membrane module. A single-membrane module consists of hundreds of thousands to more than a million micron-sized diameter hollow fibers bundled together. A couple of individual membrane hollow fibers, a small bundle loop of fibers, and modules of different sizes are shown in Figure 3. As flue gas flows through the membrane fibers, the feed is split into two streams. A permeate stream enriched in CO_2 is produced by the preferential transport of CO_2 across the fiber walls. The remaining flue gas (non-permeate) flows out of the membrane module as a CO_2-depleted retentate stream that is sent to the plant stack for discharge to the atmosphere.

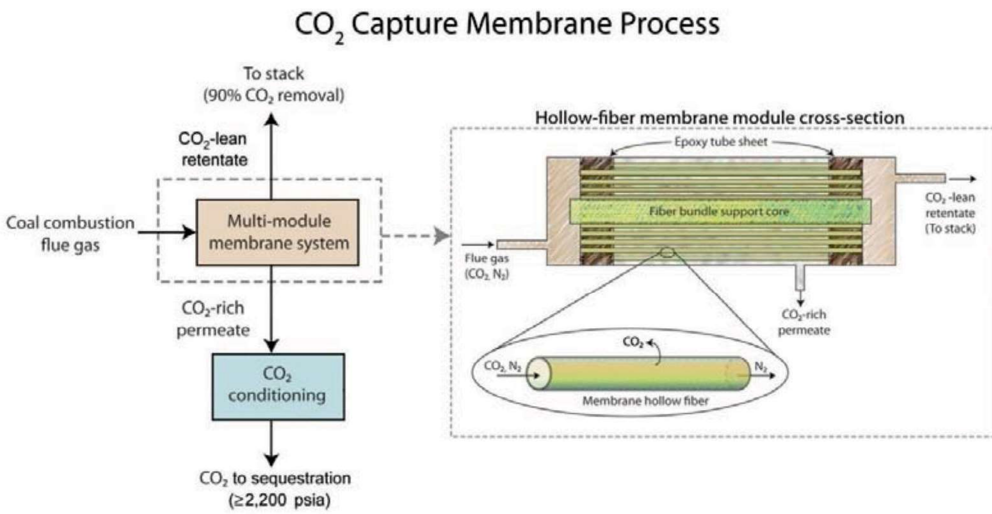

Figure 2: Cross-Section of a Hollow-Fiber Membrane Module

Individual Membrane Hollow Fibers **Small Bundle Loop of Hollow Fibers** **Various Membrane Module Sizes**

Figure 3: Membrane Hollow Fibers

Process simulations for a single-stage membrane process were conducted to determine the sensitivity of CO_2 removal performance and permeate CO_2 purity to different parameters, including membrane flux (permeance), membrane selectivity, membrane fiber dimensions, and membrane pressure driving force. An important outcome of this sensitivity analysis was the understanding that membrane property development should focus on improving both permeance and selectivity together rather than individually.

To achieve high levels of CO_2 capture and purity, RTI developed the three-stage membrane process shown in Figure 4, where the membrane stages are represented by M1, M2, and M3. The flue gas is compressed and fed to the first membrane stage M1. To obtain a net 90 percent removal of CO_2 from the stream ultimately sent to the stack, the CO_2-depleted retentate exiting M1 is fed to M3, which is operated with a permeate-side air sweep to enhance removal of more CO_2. Before being released into the stack, the pressurized M3 retentate is sent to an expander to recover the energy associated with high pressure. The resulting M3 permeate is a CO_2 enriched air stream that is sent back to the boiler. In the second membrane stage M2, the CO_2 captured in the M1 permeate is further concentrated. The resulting CO_2-rich M2 permeate is then compressed and dehydrated to produce the final, sequestration-ready CO_2 capture stream. The M2 retentate is recycled and fed back to M1. The numbers shown in Figure 4 are for a 550-MW coal-fired power plant to achieve 90 percent CO_2 capture and 95 percent CO_2 purity in the capture stream using the high-flux polycarbonate membrane (400 GPU; CO_2/N_2 = 35).

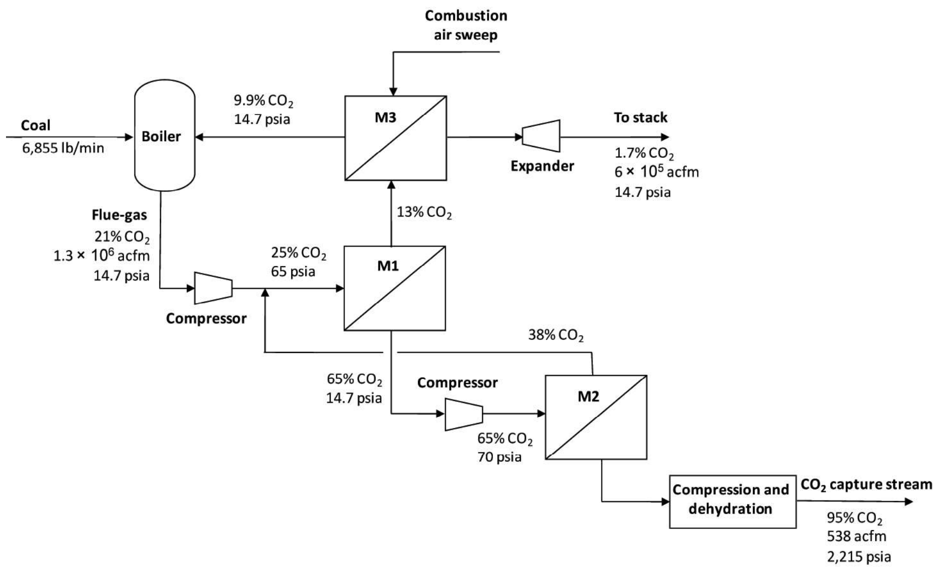

Figure 4: RTI's Three-Stage CO_2 Capture Membrane Process Design

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Polycarbonate-based and Vinylidene fluoride-based	
Materials of Fabrication for Support Layer	-	N/A	
Nominal Thickness of Selective Layer	μm	0.05	0.05
Membrane Geometry	-	Hollow-fiber	Hollow-fiber
Max Trans-Membrane Pressure	bar	15 (Not tested higher)	15
Hours Tested Without Significant Degradation	-	165	300 (coal)
Manufacturing Cost for Membrane Material	$/m^2	32	8
Membrane Performance			
Temperature	°C	25 – 30	50
CO_2 Pressure Normalized Flux	GPU or equivalent	400	1,000
CO_2/H_2O Selectivity	-	0.04	0.01 – 0.02
CO_2/N_2 Selectivity	-	35	50
CO_2/SO_2 Selectivity	-	≈1	<0.5 or >2
Type of Measurement	-	Ideal and mixed	Ideal and mixed
Proposed Module Design			
Flow Arrangement	-	Countercurrent	
Packing Density	m^2/m^3	9,000	
Shell-Side Fluid	-	Permeate	
Flue Gas Flowrate	kg/hr	(Unknown at this stage)	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 95+%, 1 bar	

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pressure Drops Shell/Tube Side	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$ / kg/hr	(Unknown at this stage)	

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 cmHg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

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 (CO_2-rich) or retentate (flue gas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Gas permeation in the high-flux polycarbonate and PVDF-based membrane platforms occurs due to a partial pressure driving force across the membrane. The specific permeation mechanism obeyed is the solution-diffusion model for gas transport in nonporous polymers. According to this model, preferential permeation of certain gas species occurs because they are more soluble in the polymer membrane, have a higher diffusion coefficient in the polymer membrane, or both. In this project, the preferentially permeated species CO_2 has both greater diffusivity and greater solubility than N_2 in the polycarbonate- and PVDF-based membranes.

Contaminant Resistance – Membrane resistance to contaminant species (NO_x, SO_2, moisture) found in flue gas was investigated in continuous, seven-day, bench-scale separation performance stability tests with contaminant-containing CO_2/N_2 mixtures. The permeance of the high-flux polycarbonate membrane showed some sensitivity to contaminants such as NO_x, but its selectivity was stable. The new PVDF-based membrane material platform, because of its intrinsically high-chemical resistance, exhibited excellent permeability (permeance) and selectivity stability in the contaminant tests.

Flue Gas Pretreatment Requirements – Before being fed to the membrane system, the flue gas from the plant stack must be conditioned to remove solid particulates and any condensed/entrained liquids (essentially liquid water).

Membrane Replacement Requirements – Based on seven-day, bench-scale contaminant resistance testing results, replacement cycle for high-flux polycarbonate membranes is anticipated to be roughly every five years. In the presence of flue-gas contaminants, the high-flux polycarbonate membrane has shown gradual permeance loss without loss in selectivity in continuous, seven-day testing. For PVDF-based membranes, the replacement cycle is anticipated to be every 10 years because of the excellent chemical and separation performance stability exhibited by them in the presence of flue-gas contaminants in seven-day tests. Much longer-term contaminant exposure testing of these membranes to real coal-derived flue gas, however, is recommended to confirm/refine the above membrane replacement requirements.

Waste Streams Generated – Because the membrane permeates and concentrates water into the CO_2 capture stream, a liquid water stream is recovered by the membrane process during compression of the capture stream to sequestration pressure. A water condensate stream is also produced upstream of membrane stages M1 and M2 because of compression of their feed gas streams, followed by cooling of this compressed gas with cooling water to the optimum membrane operating temperature. The quality of these liquid water streams is not known and will need to be determined.

technology advantages

Membrane-based processes have the potential to provide PC-fired power plants with a cost-effective technology option for CO_2 capture. They are inherently energy-efficient because the membrane enables passive separation of gases. Their compact footprint and modular nature allows for easy installation into an existing PC-fired plant, and, with no moving parts, they are simple to operate and maintain. In addition, the hollow fiber membrane approach taken in this project is particularly well suited for high-volume applications such as the large flue gas volumes that must be handled in post-combustion carbon capture. Hollow-fiber modules have much higher membrane packing density and lower cost-per-membrane area than other module types. The hollow-fiber membrane tubes are economically produced on a commercial scale by using existing fiber manufacturing equipment technology.

R&D challenges

Flue gas properties, such as low CO_2 concentration of 13 to 15 percent, low flue gas pressure of 1 atm, large flue gas volumes, and the presence of moisture and contaminants (sulfur oxides [SO_x], NO_x, and particulate matter), can pose certain challenges for a conventional membrane separation process. These technology challenges are being addressed in this project through the development of new membrane materials with improved CO_2 separation properties and chemical resistance, improved membrane module design and engineering, and novel process design and integration strategies.

results to date/accomplishments

- Development and scale-up of Generon next-generation, high-flux polycarbonate membrane hollow fibers with up to four times higher CO_2 flux (410 GPU) than that of Generon standard polycarbonate membrane fibers.
  - CO_2/N_2 selectivity of high-flux polycarbonate hollow-fiber membrane was comparable to that of standard (current-generation) polycarbonate hollow-fiber membrane. However, it was only 60 to 70 percent of its intrinsic CO_2/N_2 selectivity (35 to 37), meaning that the high-flux polycarbonate membrane properties could still be improved.
  - Fibers of high-flux polycarbonate with 25 percent larger dimensions were successfully spun as an option for managing parasitic axial pressure drops in the module.
  - High-flux polycarbonate membrane would be best operated at temperatures below room temperature to benefit from substantial increase in CO_2/N_2 selectivity without much decrease in CO_2 permeance due to its weak temperature dependence.
  - High-flux polycarbonate membrane displayed some sensitivity to flue-gas contaminants (NO_x and SO_2), which led to a permeance decline but had minimal to no effect on CO_2/N_2 selectivity. This observed sensitivity did not seem to degrade the membrane as it recovered much of its original properties when the contaminants were removed. In practice, therefore, feed pretreatment should be considered for this membrane.
- Successful formation of Generon high-flux polycarbonate membrane fibers into lab-scale modules and larger prototype (2,200 ft^2) modules.
- Development and synthesis of novel Arkema VDF-based copolymers with improved CO_2 permeance and improved CO_2/N_2 selectivity.
  - Copolymerization of a bulky, low-dipole Comonomer A into the VDF chain backbone can increase gas permeability by disrupting chain packing density and crystallinity in the polymer matrix.
  - VDF-co-A copolymer family was developed with up to 17 to 18 times higher CO_2 permeability than the base PVDF homopolymer, while maintaining the CO_2/N_2 selectivity of 24 of the base PVDF.
  - Copolymerization of a bulky, high-dipole Comonomer B into the VDF chain backbone can increase CO_2/N_2 selectivity by enhancing the CO_2 affinity of the polymer while also improving gas permeability relative to the base PVDF homopolymer.

- VDF-co-B copolymer family was developed with 2.5 to 3 times higher CO_2/N_2 selectivity and six times higher CO_2 permeability than base PVDF homopolymer.
- Strong temperature dependence of CO_2 permeance in VDF-based polymers could be exploited as a key process variable for increasing and optimizing CO_2 permeance to increase gas processing throughput in the capture process while maintaining reasonable CO_2 removal.
- VDF-based polymer platform demonstrated excellent stability of its gas separation properties to contaminants SO_2, NO_x, and water vapor.

• Fabrication of the first developmental hollow fibers from new Arkema VDF-based copolymer platform.
  - VDF-A.2 was down-selected for fiber development because it had among the best balance of CO_2 permeability and selectivity of the new copolymers in this fluorinated platform.
  - Synthesis of VDF-A.2 was successfully scaled up to pilot scale to prepare 200 pounds of this resin for fiber development.
  - Fiber tackiness, fiber shape stability, and solvent extraction kinetics were identified as key issues that must be addressed and managed for the VDF-based polymers.
  - Hollow-fiber cores of the VDF-based materials were successfully spun on commercial fiber-spinning equipment. Fibers had good gas flux but exhibited no gas selectivity. Development of a membrane structure with gas selectivity will require additional research and development (R&D) effort.

• Development of three-stage CO_2 capture membrane process design to achieve 90 percent CO_2 capture and 95 percent CO_2 purity.

• Completed techno-economic evaluation of three-stage CO_2 capture membrane process design based on Generon's high-flux polycarbonate hollow-fiber membrane assuming a CO_2 permeance of 400 GPU and CO_2/N_2 selectivity of 35.
  - Increase in levelized cost of electricity (LCOE) estimated for subcritical coal power plant with RTI membrane process was estimated to be ≈73 to 82 percent over that of a plant with no capture, with the LCOE increase depending strongly on compressor cost.
  - Compressor costs made up the majority of equipment costs for the process, with 64 percent of costs attributed to compressors needed for the CO_2 separation process and 10 percent to the compressor for compression/drying of the captured CO_2 product.
  - Cost of CO_2 capture was estimated to be ≈\$42/ton-CO_2.
  - The energy penalty was the biggest contributor to the LCOE.

next steps

This project ended on September 30, 2011.

available reports/technical papers/presentations

"CO_2 Capture Membrane Process for Power Plant Flue Gas," Final Report, April 2012. *http://www.netl.doe.gov/publications/factsheets/program/05313%20Final%20Report%20April%202012.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/22Aug11-Toy-RTI-CO2-Capture-Membrane-Process.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Lora-Toy---NT0005313.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/5313-RTI-membrane--Toy--mar09.pdf*.