CO_2 Capture Membrane Process for Power Plant Flue Gas

Lora Toy, Atish Kataria, Nandita Akunuri, and Raghubir Gupta
RTI International, Center for Energy Technology, Research Triangle Park, NC

Ramin Amin-Sanayei, Cedric Airaud, Caiping Lin, and John Schmidhauser
Arkema Inc., King of Prussia, PA

John Jensvold, Fred Coan, Raymond Chan, and Marc Straub
Generon IGS, Inc., Pittsburg, CA

2011 NETL CO_2 Capture Technology Meeting
Pittsburgh, PA

August 22, 2011

RTI International

Center for Energy Technology (CET)

Core Competencies

- Catalyst, sorbent, and membrane development
- Reaction engineering
- Process engineering design, modeling, development, and integration
- Techno-economic evaluations
- Bench-scale and prototype testing

RTI International

- Established in 1958
- One of the world's leading research institutes
- >2,800 staff; >$758MM revenue (2010)
- *Mission*: To improve the human condition by turning knowledge into practice

CET Program Areas

- Advanced Gasification
  - Warm syngas cleanup/conditioning
  - Substitute natural gas (SNG) production
  - Hydrogen production (Chemical looping)
- Biomass & Biofuels
  - Biomass gasification; Syngas cleanup/conditioning
  - Biomass pyrolysis ---> Biocrude; Conventional fuels
- Fuels & Chemicals
  - Syngas to fuels and chemicals
  - Hydrocarbon desulfurization
- Carbon Capture & Reuse
  - Pre-combustion CO_2 capture
  - Post-combustion CO_2 capture
  - CO_2 reuse for fuels/chemicals

Project Overview

DOE/NETL Cooperative Agreement #DE-NT0005313

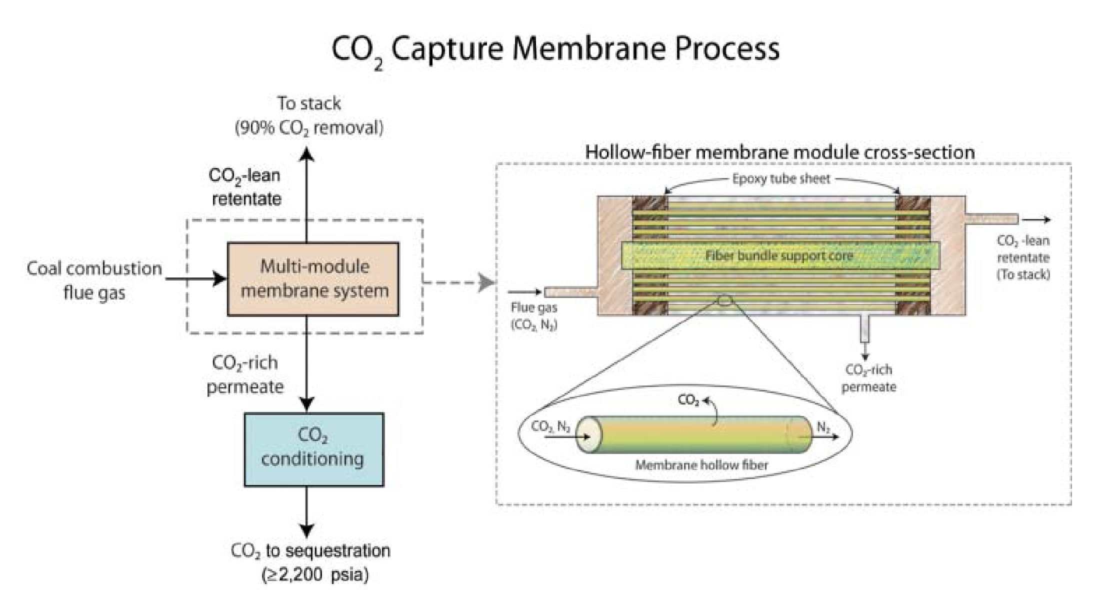
- DOE Project Manager: Andrew O'Palko
- RTI Project Manager: Lora Toy

Period of Performance

October 1, 2008 – September 30, 2011

Funding

- DOE Share: $1,944,821
- Cost Share: $486,206
- **Total Funding: $2,431,027**



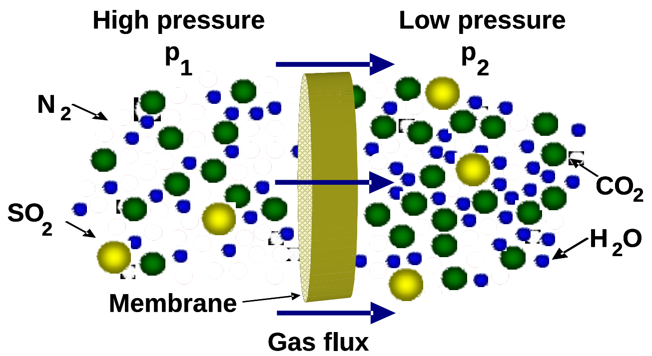
Project Team

- RTI
- Arkema Inc.
- Generon IGS, Inc.

Overall Project Objective

Develop an advanced polymeric membrane-based process that can be cost-effectively retrofitted into existing pulverized coal plants to capture ≥ 90% CO_2 from plant flue gas with ≤ 35% Increase in Cost of Electricity (ICOE)

Membrane Approach



Solution-diffusion mechanism

(i) Sorption on high-pressure side
(ii) Diffusion down partial pressure gradient
(iii) Desorption on low-pressure side

$$P = S \times D$$

Permeability (P), **Solubility** (S), **Diffusivity** (D)

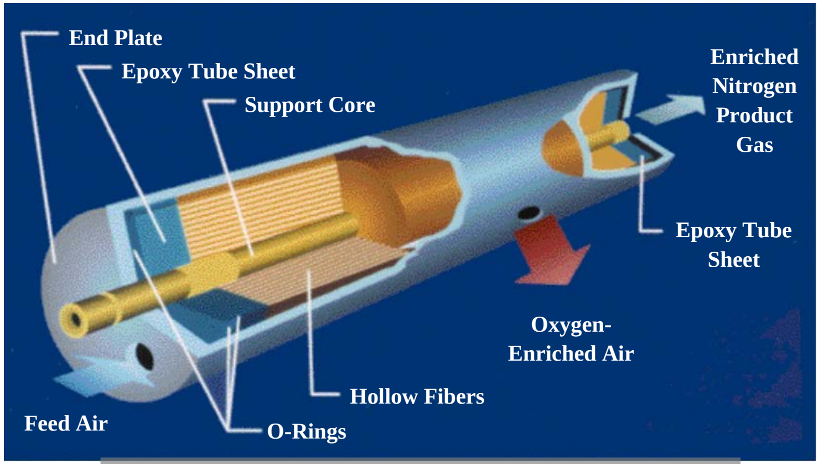
$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} = \left(\frac{S_{CO_2}}{S_{N_2}}\right)\left(\frac{D_{CO_2}}{D_{N_2}}\right)$$

Selectivity (α_{CO_2/N_2}), **Solubility selectivity** (S_{CO_2}/S_{N_2}), **Mobility selectivity** (D_{CO_2}/D_{N_2})

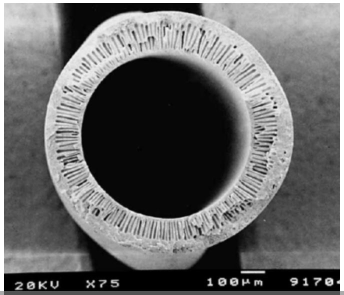
Advantages

- Passive separation
  - Inherently energy-efficient
  - No heating needed to recover CO_2 (unlike adsorption and absorption processes)
- Simple to operate and maintain
  - No moving parts
- Compact
- Modular
  - Easy scalability
  - Easy to retrofit into existing process infrastructures
- No secondary hazardous waste stream

Hollow-Fiber Membrane Modules for High-Volume Applications



Typical design of Generon hollow-fiber membrane module



Cross-section of typical polymeric hollow-fiber membrane
[From Koops et al., *J. Appl. Polym. Sci.*, 54, 385 (1994)]

Common Membrane Module Designs Used for Gas Separations

Characteristic	Spiral-wound	Hollow-fiber
Membrane form	Flat sheet	Hollow fiber
Packing density (ft^2/ft^3)	300-1,000	3,000-5,000
Cost ($/$ft^2$)	1-5	0.2-1
Area of std. module (ft^2)	200-640	3,000-7,000

Ref. Baker, R. W., "Membrane Technology and Applications", 2nd ed., John Wiley and Sons: West Sussex, England, 2004, pp. 89-160.

Hollow-fiber module type selected

- *Lower module cost per membrane area*
- *Much higher membrane packing density*
- *More suitable and cost-effective for high-volume applications (e.g., air separation)*

Hollow-Fiber Membrane Module Cost

Comparison to Spiral-Wound

Genereon module fabrication

Generon module sizes
100-10,000 ft^2 (10-1,000 m^2)

Example Membrane Module Cost Comparison

(550-MWe coal plant; 90% capture; 95% CO_2 purity; $\alpha_{CO2/N2}$ = 35; 1.3 × 10^6 acfm)

	Spiral-wound	Hollow-fiber
Membrane area	2.6 10^7 ft^2 (400 GPU) 1 10^7 ft^2 (1,000 GPU) 2.6 10^6 ft^2 (4,000 GPU)	2.6 10^7 ft^2 (400 GPU)
Area per module[a]	1,163 ft^2	2,200 ft^2
No. of modules	22,356 (400 GPU) 8,599 (1,000 GPU) 2,236 (4,000 GPU)	11,819 (400 GPU)
Module cost (installed)[b]	\$4.65/ft^2	\$1.05/ft^2
Total module cost	\$121MM (400 GPU) \$46.5 MM (1,000 GPU) \$12.1 MM (4,000 GPU)	\$27.3MM (400 GPU)

[a] *Assumed standard module size of 8 in. × 40 in. for spiral-wound and 6 in. × 36 in. for hollow-fiber.*

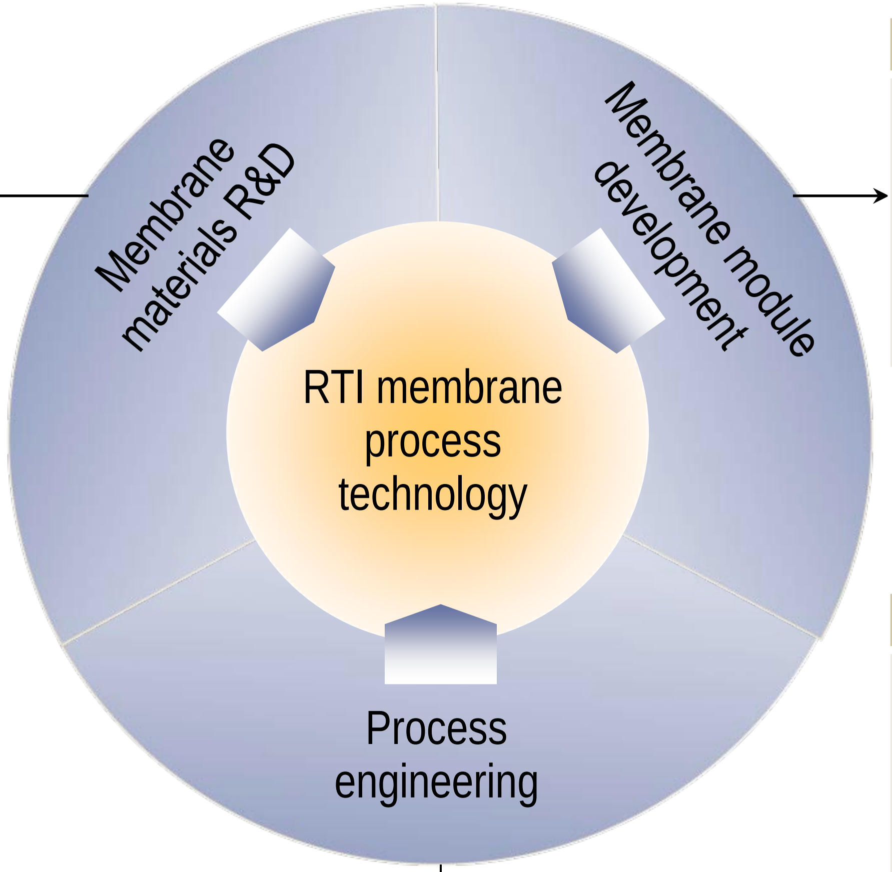
[b] *Cost for spiral-wound from Merkel et al. [J. Membr. Sci., 359, 126-139 (2010)] and for hollow-fiber from project partner Generon.*

For the same membrane permeance and selectivity, the hollow-fiber design is much more cost-effective than spiral-wound.

RTI's CO_2 Capture Membrane Process Development

Membrane Materials

- CO_2 permeability (i.e., permeance or flux)
- CO_2/N_2 selectivity
- Contaminant resistance
- Processability into membrane structures



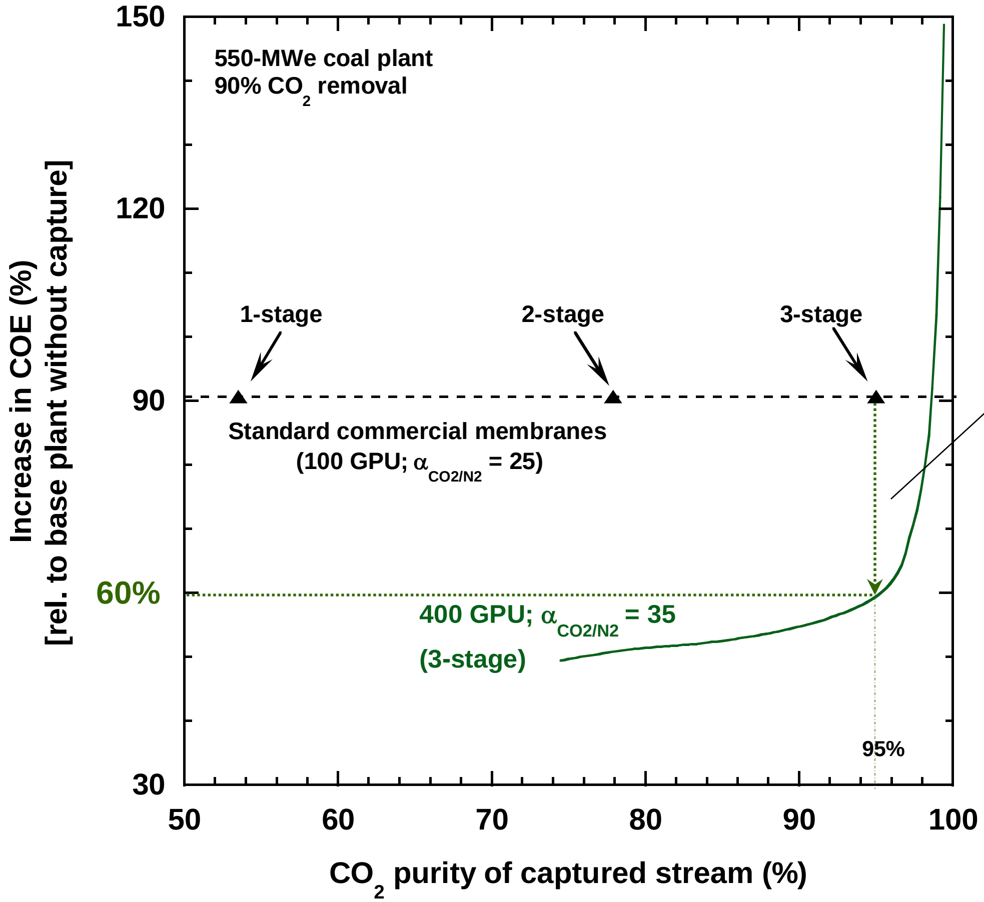
Membrane Modules

- Membrane fiber/module manufacturability
- Membrane sealing in module shell
- Pressure drop effects
- Gas flow distribution

Process engineering

- Process design and development
- Process integration
- Techno-economic evaluation (capture costs; ICOE)

Project Progress – Part 1

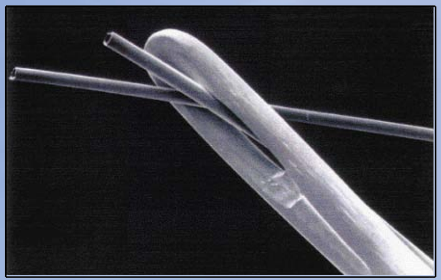


Key Enabling Developments

- Promising 3-stage membrane process design
- Generon high-flux polycarbonate (PC)
  - Formation/Production of membrane hollow fibers
  - Construction of membrane modules from membrane hollow fibers [From lab to larger prototypes (6 in. x 36 in.)]

Basis of ICOE calculations: "*Cost and Performance Baseline for Fossil Energy Plants*", Vol. 1: Bituminous Coal and Natural Gas to Electricity Final Report, DOE/NETL-2007/1281, August 2007.

Generon Polycarbonate (PC) Membrane Platform
Next-Generation, High-Flux PC vs. Standard PC



Individual Generon hollow membrane fibers

Generon lab-scale hollow-fiber membrane modules

- Membrane hollow fibers from high-flux PC were successfully formed.
  - Mechanically durable up to at least 10,000 pressure cycles at 135 psig minimum pressure
- New high-flux PC fibers spun have
  - CO_2 permeance **4 times faster** than that of standard PC fibers
  - CO_2/N_2 selectivity similar to that of standard PC fibers

Hollow-fiber module	Gas permeance (GPU)				Gas selectivity		
	N_2	O_2	CO_2	SO_2	O_2/N_2	CO_2/N_2	SO_2/N_2
Standard PC	4.0	26	100	130	6.5	25	32
High-flux PC*	19	100	410	575	5.3	22	30

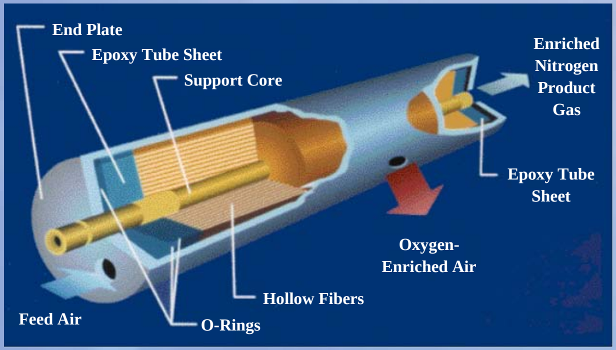
* Intrinsic CO_2/N_2 selectivity obtained on high-flux PC films was 35-37.
1 GPU = 1×10^{-6} $cm^3(STP)/(cm^2 \cdot s \cdot cmHg)$

- Fibers with 25% larger dimensions were also successfully spun as an option for mitigation of pressure drops (50% lower).
- Production of larger prototype modules (6 in. × 36 in.) with properties similar to the smaller lab-scale modules was completed recently.

Membrane Module Development Efforts

Key Design Considerations

- Dimensions of hollow fiber and module device
  - Minimize parasitic pressure drops (i.e., maximize pressure driving force)
  - Able to handle high-volume flue-gas flows
- Gas ports on module
  [e.g., 3-port or 4-port (with sweep); location]
- Gas-tight sealing of membrane hollow fibers in module housing
  - Formulation of epoxy tubesheet potting resin (compatible with flue-gas environment and membrane)
  - Isolation of feed side from permeate side of membrane
  - Potting seal of fiber bundle with module shell
- Fiber bundling and packing density
  - Fiber weave arrangement in hollow-fiber fabric
  - Uniform gas distribution
  - Minimize channeling, bypassing, and stagnant regions



Typical design of Generon hollow-fiber membrane module

Generon high-flux PC membrane fibers were successfully formed into larger prototype, 2,200-ft^2 modules having the same separation properties as that measured on lab-scale modules.

Process Design and Engineering

Integration Parameters Considered

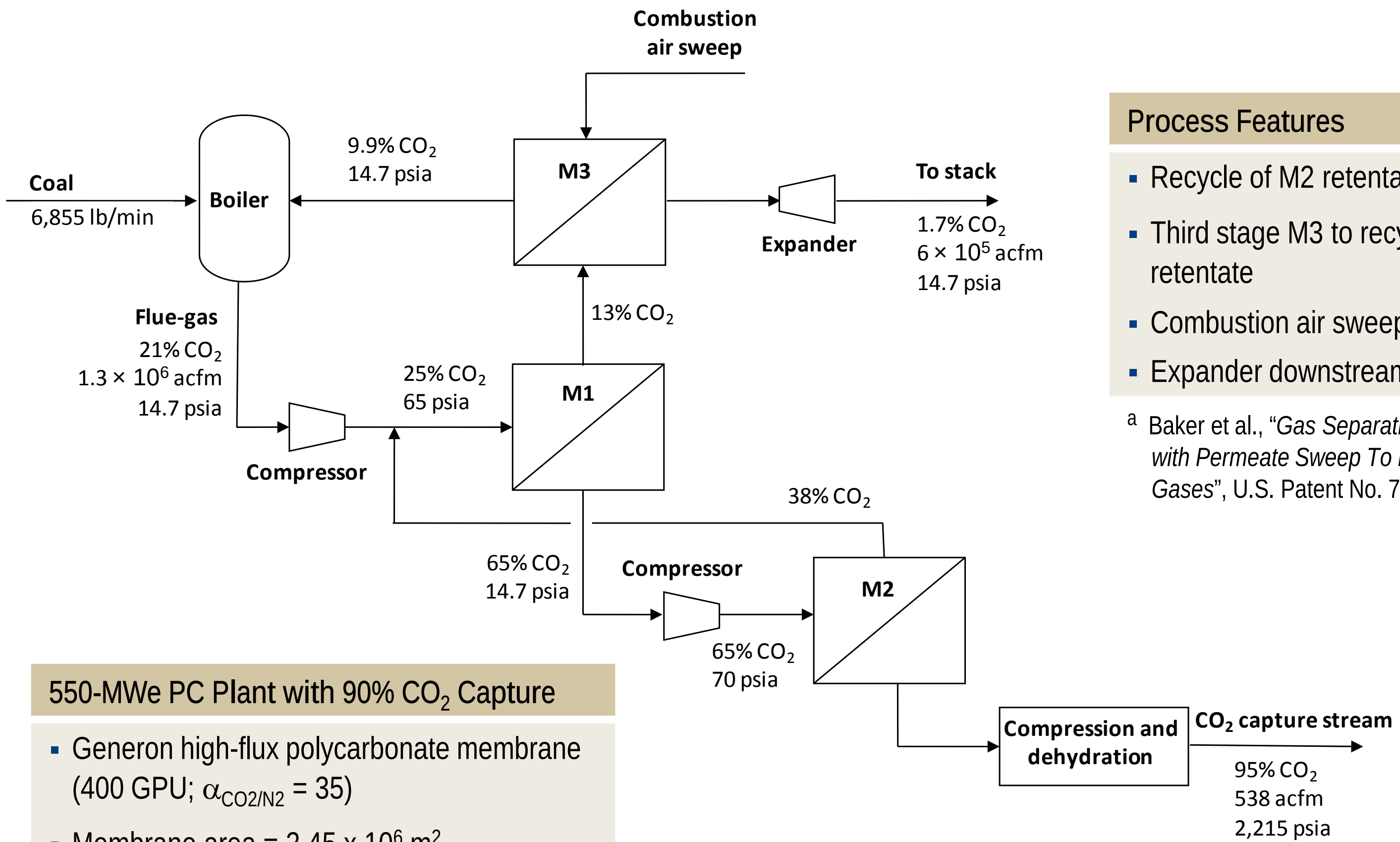
Objective

Demonstrate techno-economic feasibility of hollow-fiber membrane capture process to achieve 90% CO_2 capture and 95% CO_2 purity

Approach

- Identify suitable process configuration(s)
  - Multi-step and multi-stage process designs (e.g., 1- to 4- stages)
  - Recycle loops and level of recycle
  - Permeate sweep
- Optimize process and operating costs
  - Dependent on membrane area requirement
    [i.e., membrane properties (permeance, selectivity)]
  - Dependent on process parameters
    [e.g., stream pressure (compression/vacuum); stage-cut; etc.]
- Maximize power and heat management
  - Minimize parasitic energy losses (e.g., compression energy)
  - Expander power recovery
  - Heat recovery from compressed streams

RTI 3-Stage Membrane Process Design



Process Features

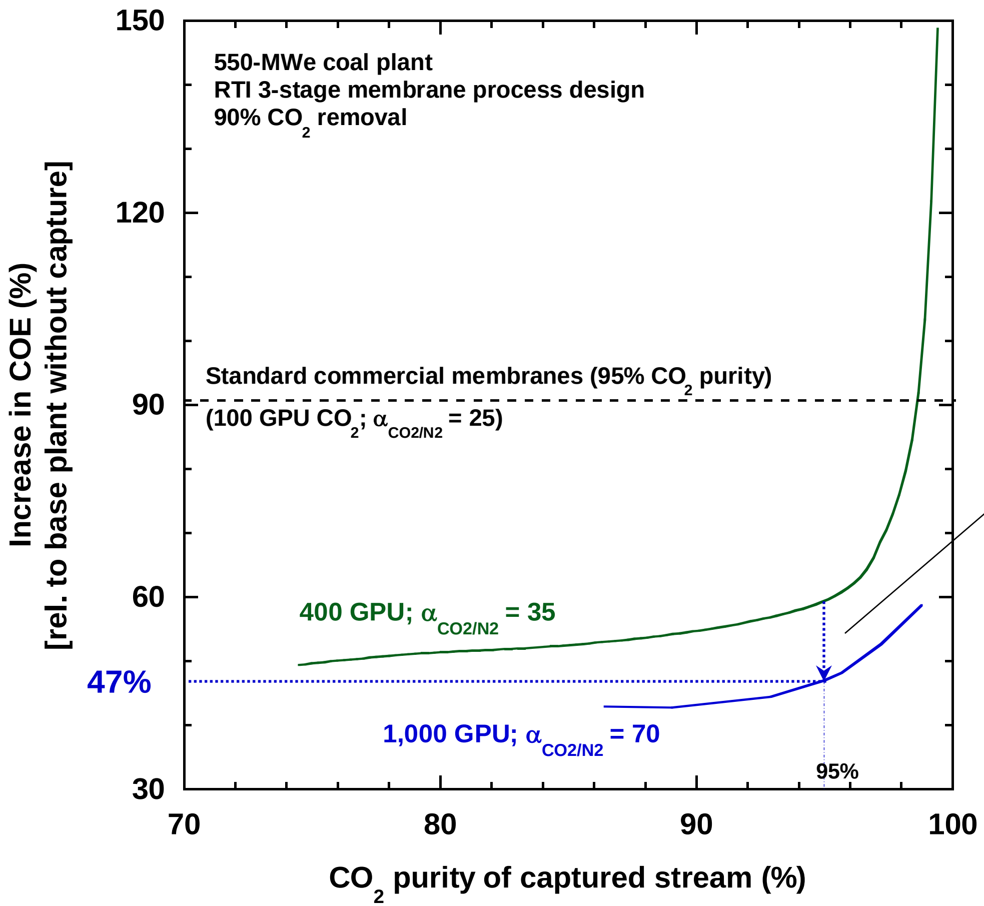
- Recycle of M2 retentate to M1
- Third stage M3 to recycle and concentrate M1 retentate
- Combustion air sweep on M3[a]
- Expander downstream of M3 (power recovery)

[a] Baker et al., "*Gas Separation Process Using Membranes with Permeate Sweep To Remove CO_2 from Combustion Gases*", U.S. Patent No. 7,964,020 (2011).

550-MWe PC Plant with 90% CO_2 Capture

- Generon high-flux polycarbonate membrane (400 GPU; $\alpha_{CO2/N2} = 35$)
- Membrane area = 2.45 x 10^6 m^2
- ICOE = 59%
- \$30/ton CO_2 captured
- \$42/ton CO_2 avoided

Project Progress – Part 2
Toward Further Reduction in COE



Accomplishments

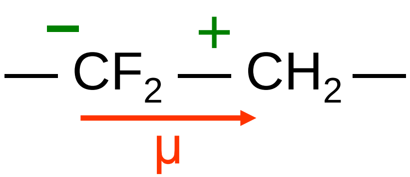
- Development/Synthesis of novel Arkema fluorinated copolymers
  - Poly(vinylidene fluoride) [PVDF] as base platform for next-generation membrane material
  - More robust materials for potentially longer-life membranes
  - Copolymerization technique to tailor polymer microstructure and, in turn, gas separation properties
    - Comonomer A increased CO_2 permeation in base polymer by 17-18 times with no adverse impact on CO_2/N_2 selectivity.
    - Comonomer B increased CO_2 permeation in base polymer by 6-10 times, accompanied by 2.5-3 times higher CO_2/N_2 selectivity.

PVDF-Based Membrane Material Platform

Arkema

Polyvinylidene fluoride (PVDF)-based polymers

- High oxidation resistance
  - Used in O_2/H_2 fuel cell membrane compositions
- High chemical resistance to acids
  - Withstands nitric acid exposure with no dimensional changes and weight loss
- Ease of processing (solution or melt)
  - Used for water purification as porous hollow fibers
- Specific affinity for CO_2
  - High CO_2 solubility due to high polar nature of VDF repeat unit

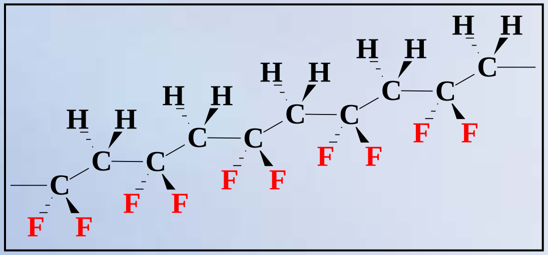


High dipole moment ⟶ Highly polar

PVDF homopolymer

- Highly crystalline (up to 50-65%), reducing gas transport
- Low CO_2 permeance ~ 5 GPU* (for 0.1-µm thickness)
- Moderate CO_2/N_2 selectivity ~ 23*

PVDF repeat unit: $–[CH_2\text{-}CF_2]_n–$



* From El-Hibri and Paul, *J. Appl. Polym. Sci.*, Vol. 31, 2533 (1986).
1 GPU = 1 × 10^{-6} $cm^3(STP)/(cm^2{\cdot}s{\cdot}cmHg)$

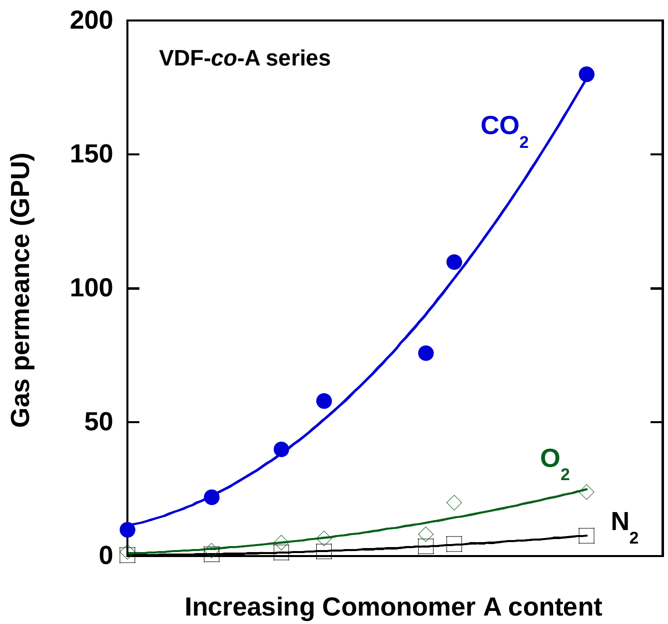
Copolymerization Approach

Arkema

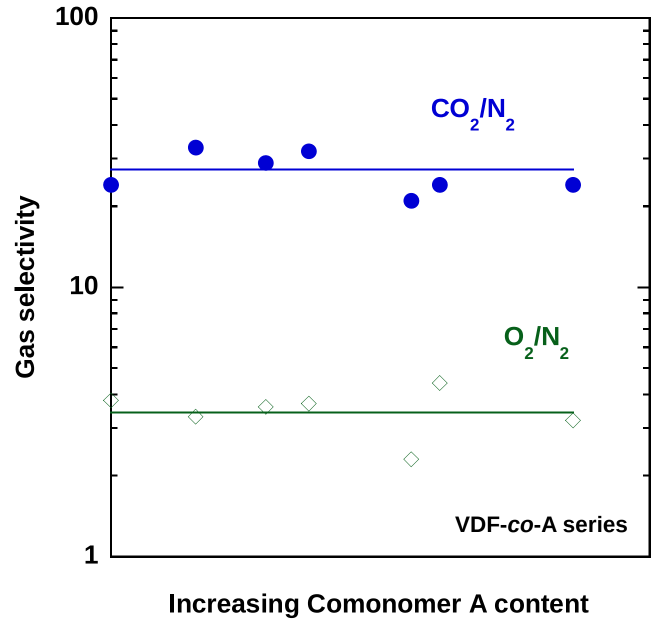
- PVDF backbone can be chemically modified.
  - To increase permeability by lowering crystallinity
  - To have higher CO_2 selectivity by changing backbone dipole moments
- Copolymerize fluoro-comonomers with bulky pendant groups into VDF backbone
  - Bulky comonomer disrupts polymer-chain organization, reducing crystallinity (down to <2%)
  - Intrinsic gas permeability of PVDF increases
  - Bulky perfluorinated Comonomer A successfully synthesized into VDF backbone
- Incorporate comonomers having greater dipole moments
  - Enhances polymer affinity for CO_2 to raise intrinsic CO_2/N_2 selectivity
  - VDF copolymers with very polar, bulky Comonomer B successfully made
    - Dipole of Comonomer B >> Dipole of Comonomer A

VDF-Based Copolymers: CO_2 Permeance Improvement

Gas permeance



Gas/N_2 selectivity



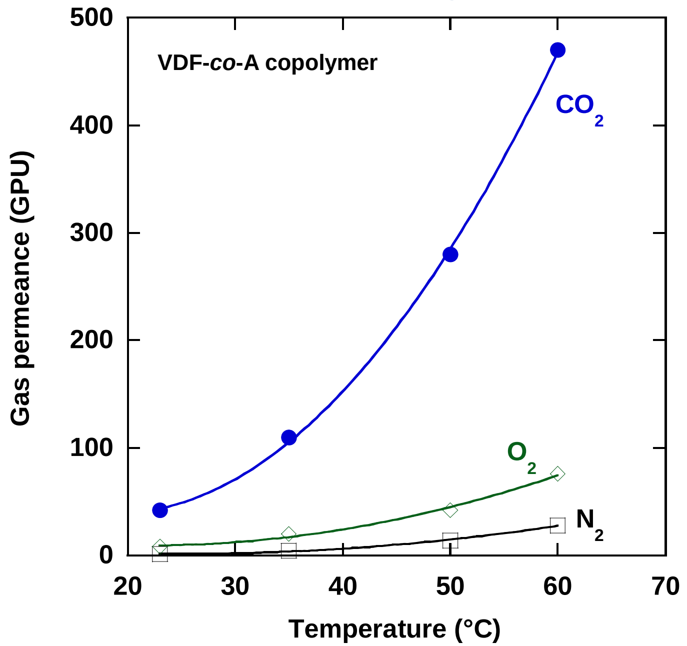
T = 35 °C; 1 GPU = 1 × 10^{-6} cm^3(STP)/(cm^2·s·cmHg)

Addition of bulky Comonomer A into the VDF backbone resulted in

- *18-fold increase in CO_2 permeance*
- *No adverse impact on CO_2/N_2 selectivity*

VDF-Based Copolymers: Effect of Temperature and More Polar Bulky Comonomer

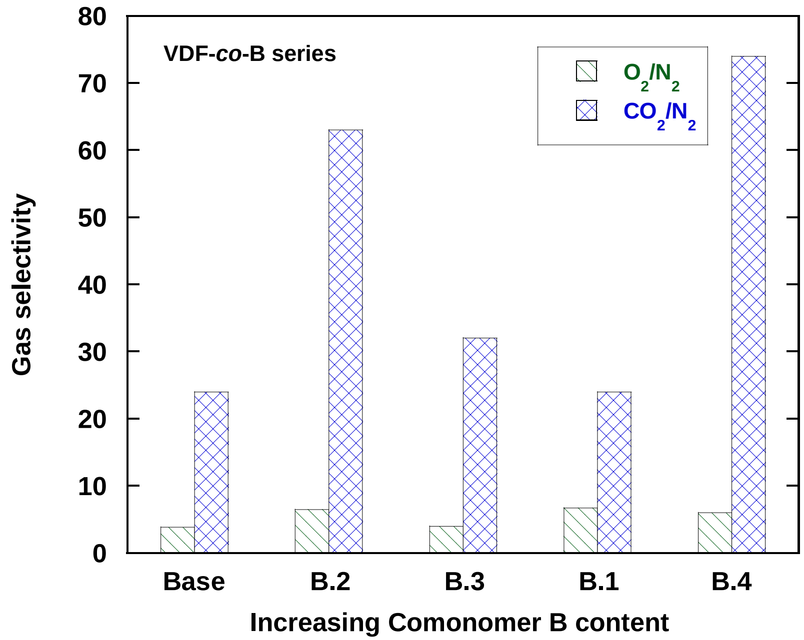
Permeance vs. temperature



1 GPU = 1 × 10^{-6} cm^3(STP)/(cm^2·s·cmHg)

- Substantial 10-fold increase in CO_2 permeance (>450 GPU) over only a small 35 C temperature interval

More polar comonomer on selectivity



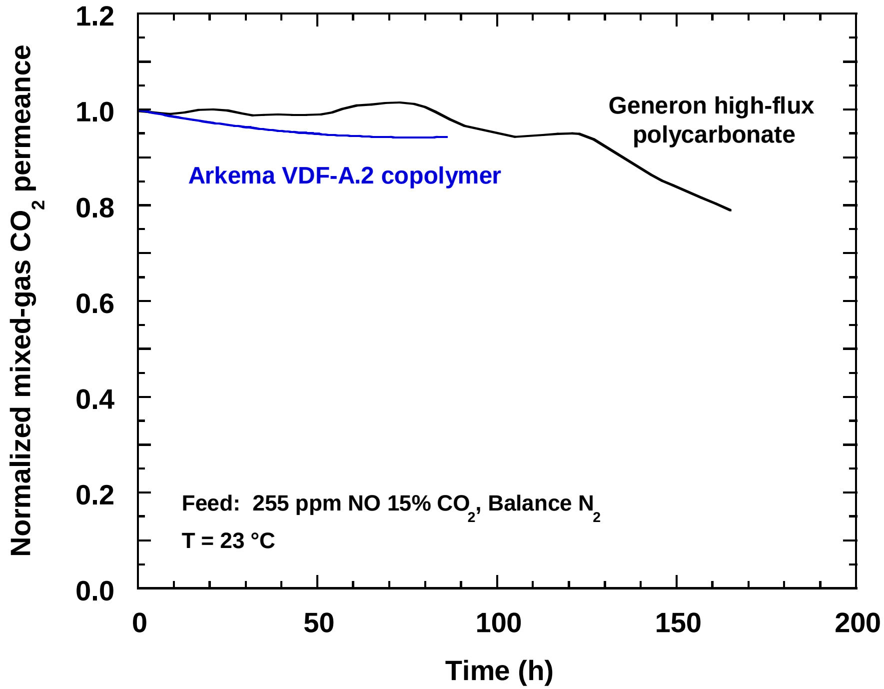
- 2.5-3 times higher CO_2/N_2 selectivity (>70), accompanied by 6-fold increase in CO_2 permeance

VDF-based copolymer properties can be tuned/optimized through process conditions (e.g., temperature) and proper comonomer selection and addition into chain backbone.

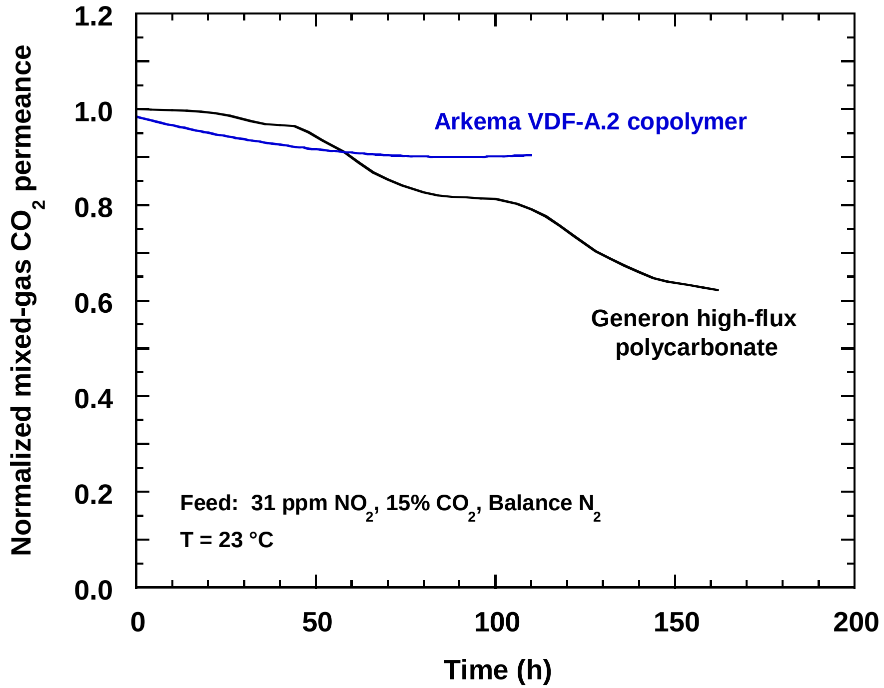
Effect of NO and NO_2 on CO_2 Permeance

Generon High-Flux PC vs. Arkema VDF-Based Copolymer

255 ppm NO in CO_2/N_2 feed



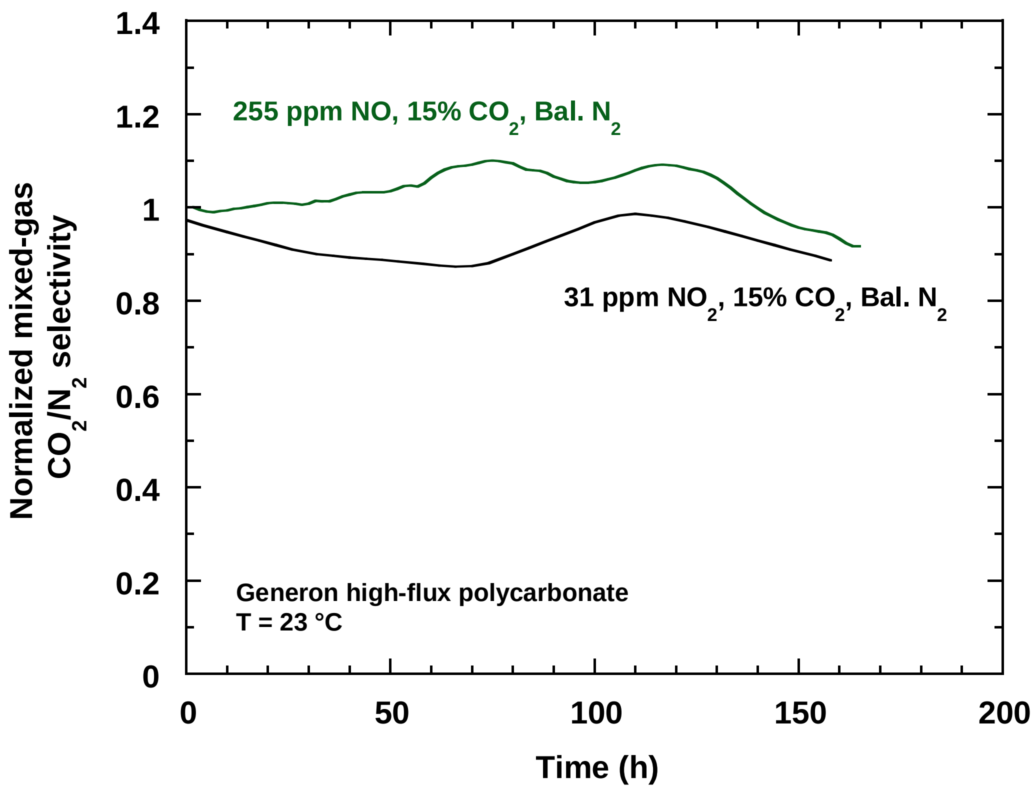
31 ppm NO_2 in CO_2/N_2 feed



VDF-based copolymers are less sensitive to NO_x than high-flux PC.

Effect of NO and NO_2 on CO_2/N_2 Selectivity

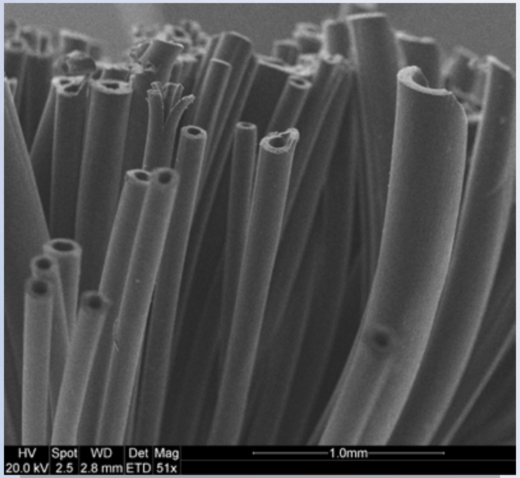
Generon High-Flux PC



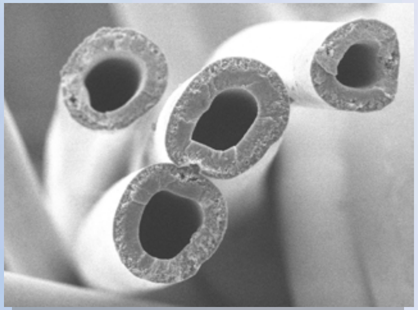
No selectivity loss occurs in high-flux PC in presence of NO_x.

VDF-Based Hollow-Fiber Membrane Development Progress – 1

- Downselection of Copolymer VDF-A.2 for developing into membrane hollow fibers
  - Comonomer A content ~ 24%
  - Higher chemical resistance than that of high-flux PC
  - Best balance of CO_2 permeability and selectivity among the new Arkema polymers (i.e., best potential of forming into membrane fibers with separation properties similar to that of high-flux PC)
- Scale-up of VDF-A.2 synthesis and preparation (200-250 lbs)
- Six VDF-A.2 fiber spin runs completed to date at Generon
  - Spin dope formulation range developed with suitable spinning characteristics and for fiber shape stability and fiber tackiness reduction
  - First-round spin process conditions identified for making stable hollow fibers (draw speed, die temperature, quench bath type and temperature)



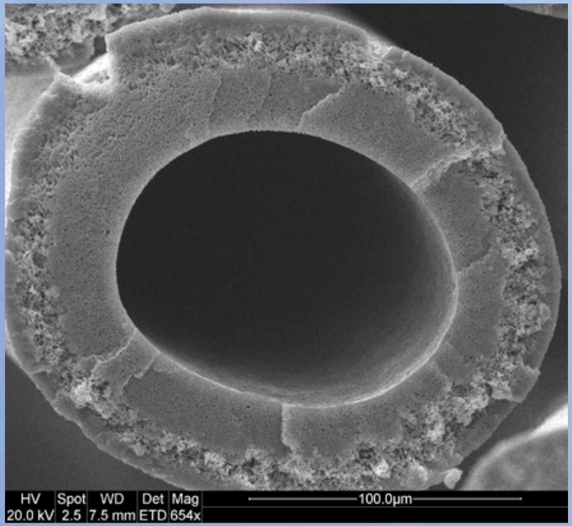
SEM of VDF-A.2 hollow fibers spun



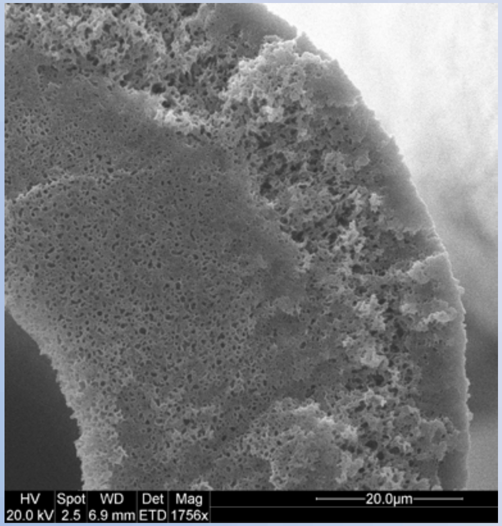
SEM cross-section
of several VDF-A.2 hollow fibers

VDF-Based Hollow-Fiber Membrane Development Progress – 2

- Evaluation in progress of first-round batches of VDF-A.2 hollow fibers
  - Structural characterization via scanning electron microscopy (SEM)
  - Formation of small lab beaker modules from fibers
  - Preliminary gas permeation testing in progress



X-section of single VDF-A.2 hollow fiber



Magnified X-section of VDF-A.2 fiber wall

Summary

- Development and synthesis of Arkema VDF-based copolymers with improved CO_2 permeance and improved CO_2/N_2 selectivity
  - 17-18 times higher CO_2 and permeability than base polymer; No adverse impact on base CO_2/N_2 selectivity (VDF-*co*-A)
  - 2.5-3 times higher CO_2/N_2 selectivity and 6 times higher CO_2 permeability than base polymer (VDF-*co*-B)
  - No detrimental interaction effect of SO_2 and NO_x on Arkema copolymers
- Development in progress of most promising Arkema VDF-based copolymer downselected for developing into membrane hollow fibers
- Development and scale-up of Generon high-flux polycarbonate (PC) membrane fibers with up to 4 times higher CO_2 flux than that of Generon standard PC fiber
- Successful formation of high-flux PC fibers into good lab-scale modules and larger prototype modules
- Identification of promising 3-stage CO_2 capture membrane process design to achieve 90% CO_2 capture and 95% CO_2 purity

Next Steps


Dedicated Research Spin Lines for Hollow-Fiber Development (2,000 ft^2)


Membrane hollow fibers


Module Manufacturing


Generon® module sizes 100-10,000 ft^2 (10-1,000 m^2)

- Complete development of Arkema VDF-based copolymer into hollow-fiber membrane with gas separation properties
  - Optimize fiber spin process conditions (skinned asymmetric structure; fiber size distribution)
  - Measure gas separation properties of new VDF-based fibers
- Update techno-economic analysis of “best” integrated/retrofitted CO_2 capture membrane process package in pulverized coal plant using best membrane properties obtained in this project

Acknowledgements

U.S. DOE/NETL

- Andrew O’Palko
- José Figueroa
- Lynn Brickett
- Jared Ciferno

Other RTI Engineering guidance/ Technical support

- Aqil Jamal
- Ranjeeth Kalluri