ADVANCED MEMBRANE TECHNOLOGIES FOR CO_2 CAPTURE AND UTILIZATION

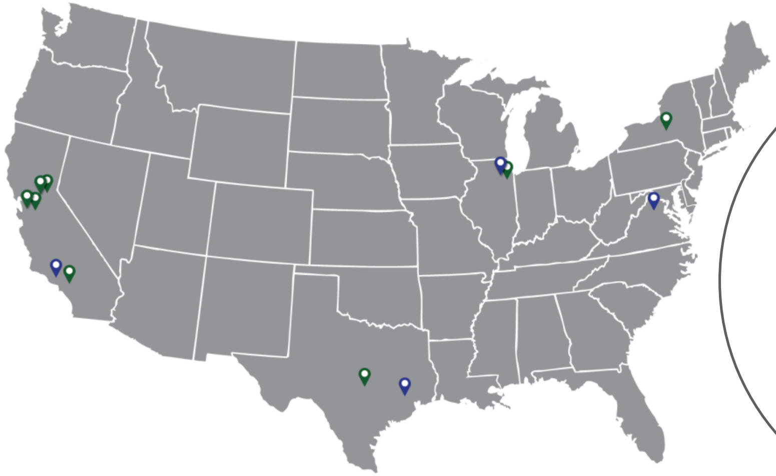
Howard S. Meyer, Shiguang Li, Naomi Klinghoffer, Travis Pyrzynski: GTI
Yong Dong: Air Liquide Advanced Separations
Miao Yu: Rensselaer Polytechnic Institute

June 2019

Trondheim CCUS Conference

Introduction to GTI

- Research organization, providing energy and environmental solutions to the government and industry since 1941
- Facilities: 18 acre campus near Chicago



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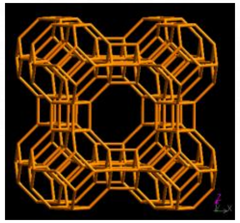
SUBSIDIARY

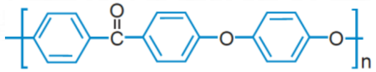
- Idea
- Market Analysis
- Technology Analysis
- Product Development
- Lab and Field Testing
- Demonstration
- Commercialization

For additional information contact Markus Lesemann (Chicago) at MLesemann@gti.energy or Eric Lei (Beijing) at Elei@gti.energy

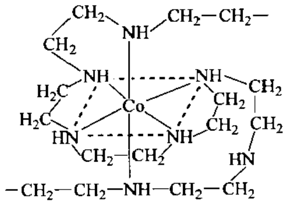
Experience: Advanced materials and innovative processes for energy and environmental relevant applications

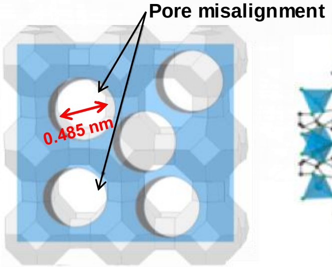
Development of advanced materials and structures for energy and environmental relevant applications


Molecular sieves

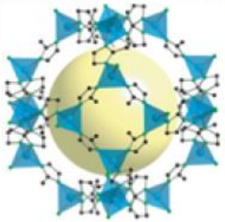


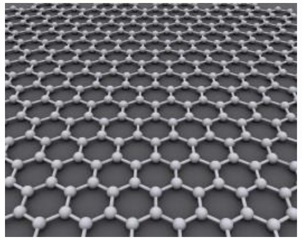
Polymers


Solvents

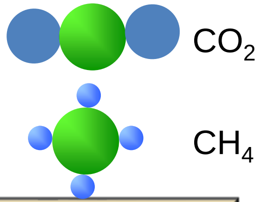


Size-Sieving Sorbents

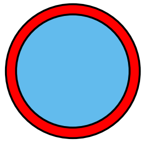

MOFs

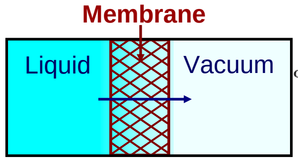

Graphene oxides

Application

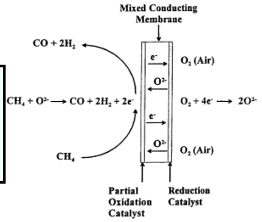


Gas separation

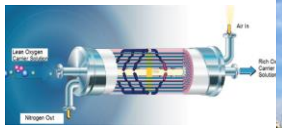

Gas storage



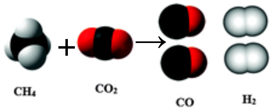
Pervaporation



Membrane reactors


Air separation

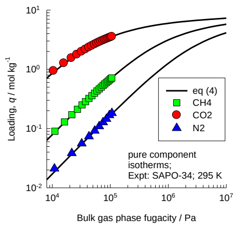

Carbon capture



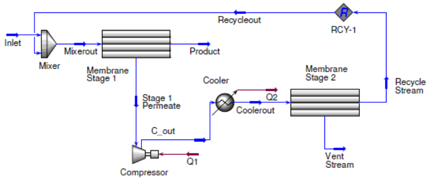
CO_2 utilization

Scale up from lab-scale to pilot plants

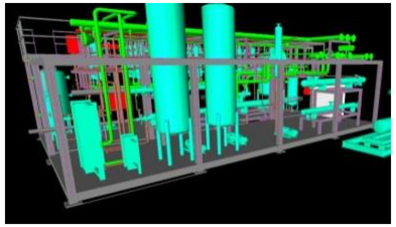

Membrane Scale-up

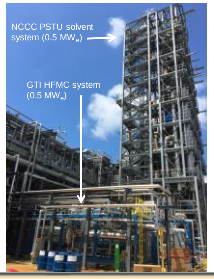


Performance modeling



Process design & economics


Design & construction of field testing unit



Pilot plant testing

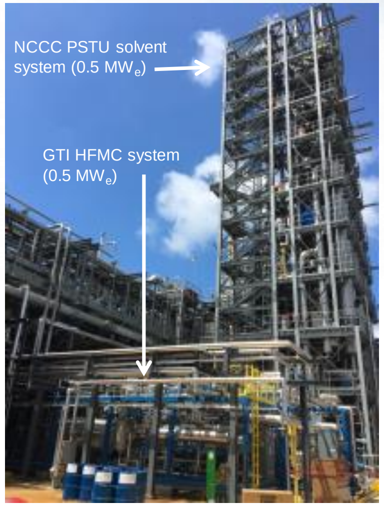
Expertise on CCUS

- **1st Gen CO_2 capture technology CarboLock™**: Currently in BP4 of piloting a 10 tonne/day CO_2 capture system at the National Carbon Capture Center (NCCC), targeting \$40/tonne of CO_2 captured, supported by US DOE

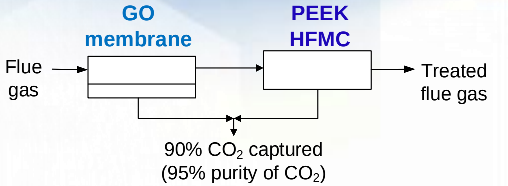
- **2nd & 3rd Gen technologies** supported by US DOE targeting \$30-35/tonne of CO_2 captured

Gen	Project	Current scale	Cost target (per tonne of CO_2 captured)
2nd	GO-PEEK	Lab	\$35
3rd	GO^2	Bench	\$30
3rd	Rota-Cap	Bench	\$30
3rd	Sorbent	Bench	\$30

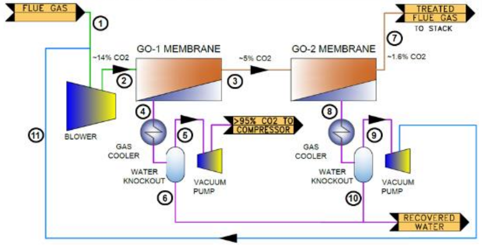
- Four CO_2 utilization technologies (dry reforming, e-beam, DME production, and DMC production) supported by US DOE



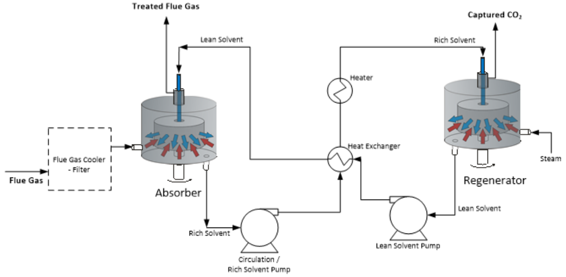
HFMC



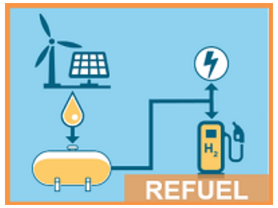
GO-PEEK



GO^2

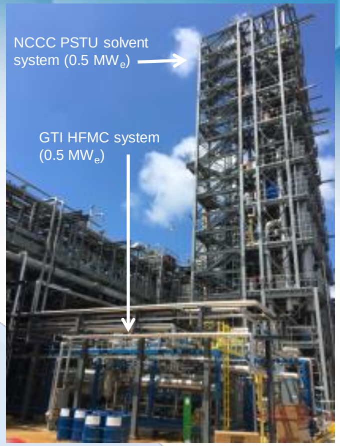


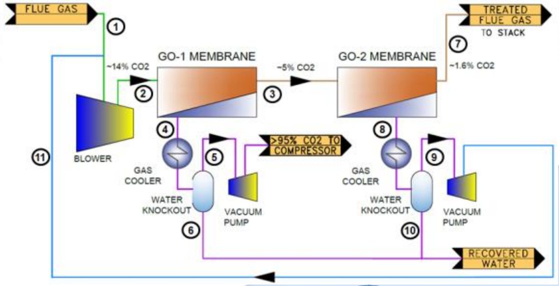
Rota-Cap

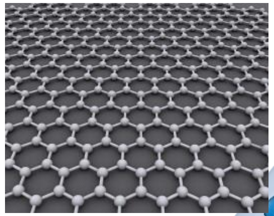


ARPA-E REFUEL

Capabilities: R&D from Concept to Pilot Plant







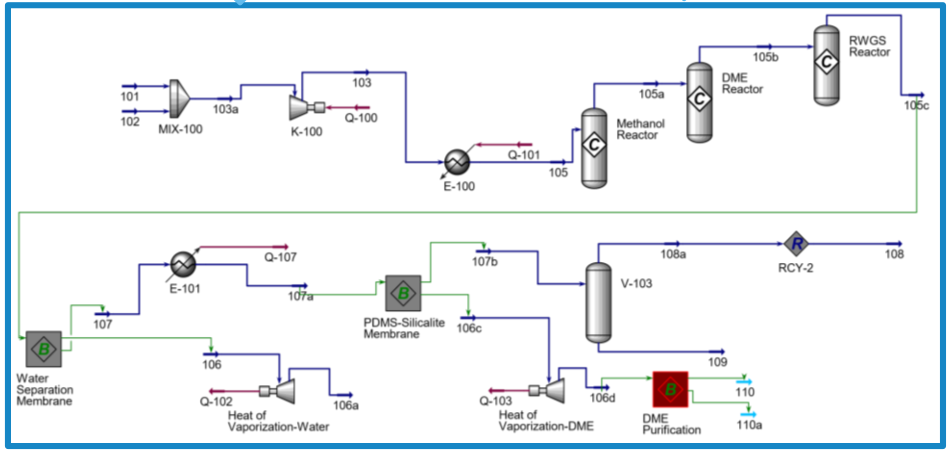
Pilot plant design and testing

Bench-scale process laboratory and field tests

Process design and package

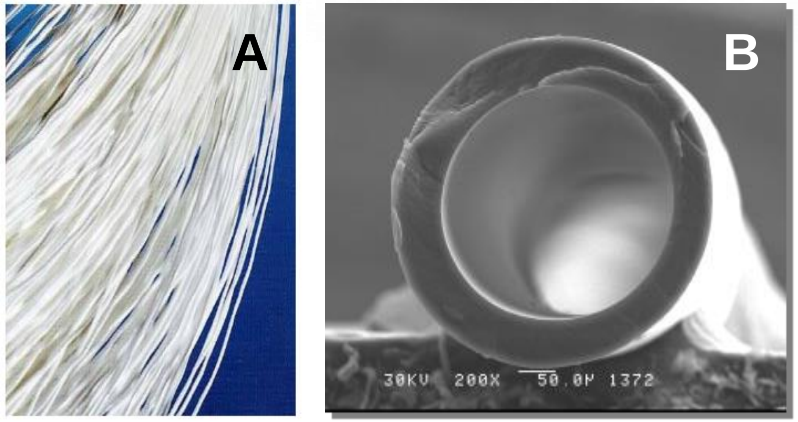
Component or/and system validation in laboratory environment

Technology concept



Modeling/ Simulation

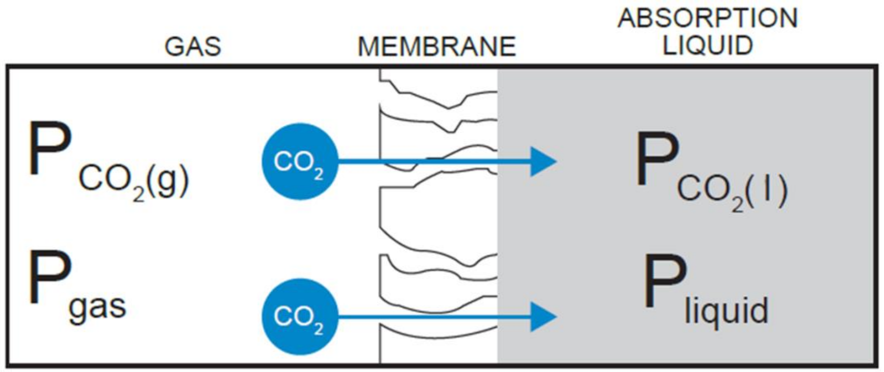
1st Gen Technology: Hollow Fiber Membrane Contactor (HFMC)

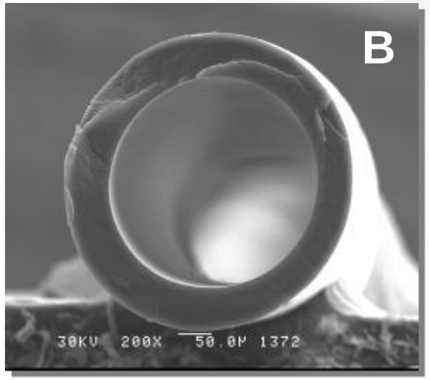


- **<u>Objectives</u>**: Build a 0.5 MW_e pilot-scale CO_2 capture system and conduct tests on flue gas at the National Carbon Capture Center (NCCC), and demonstrate a continuous, steady-state operation
- **<u>Team</u>**: gti AIR LIQUIDE ADVANCED BUSINESS & TECHNOLOGIES ALaS PoroGen INNOVATIVE MEMBRANE PRODUCTS PEEK inside TRIMERIC CORPORATION NATIONAL CARBON CAPTURE CENTER

Singular PEEK HFMC technology currently at 0.5 MW_e pilot scale development stage (DE-FE0012829)

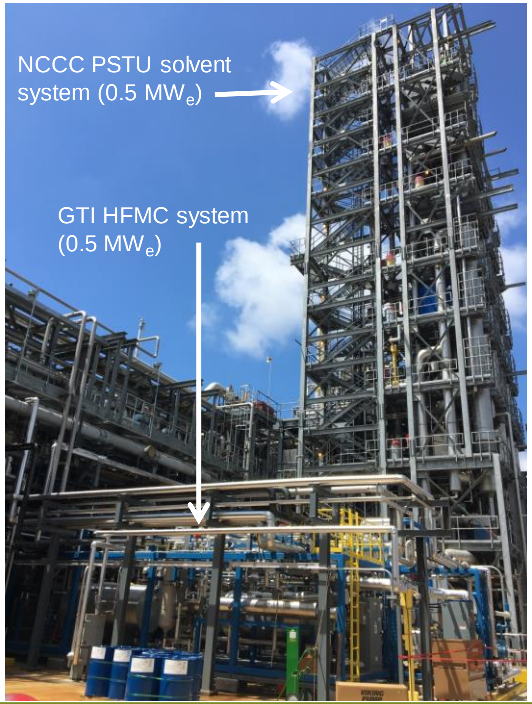
Membrane contactor: high surface area device that facilitates mass transfer





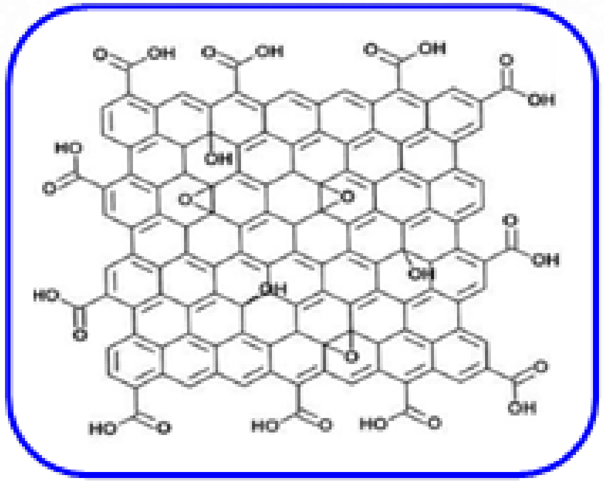
PEEK made into hollow fibers with high packing density

Commercial-sized (8-inch-diameter) modules with intrinsic CO_2 permeance of ~2,000 GPU used in pilot scale testing



Plant constructed, installed and being tested at NCCC
12 m (L) x 7.5 m (W) x 3.5 m (H)

2nd Generation Technology: GO-HFMC Hybrid Process



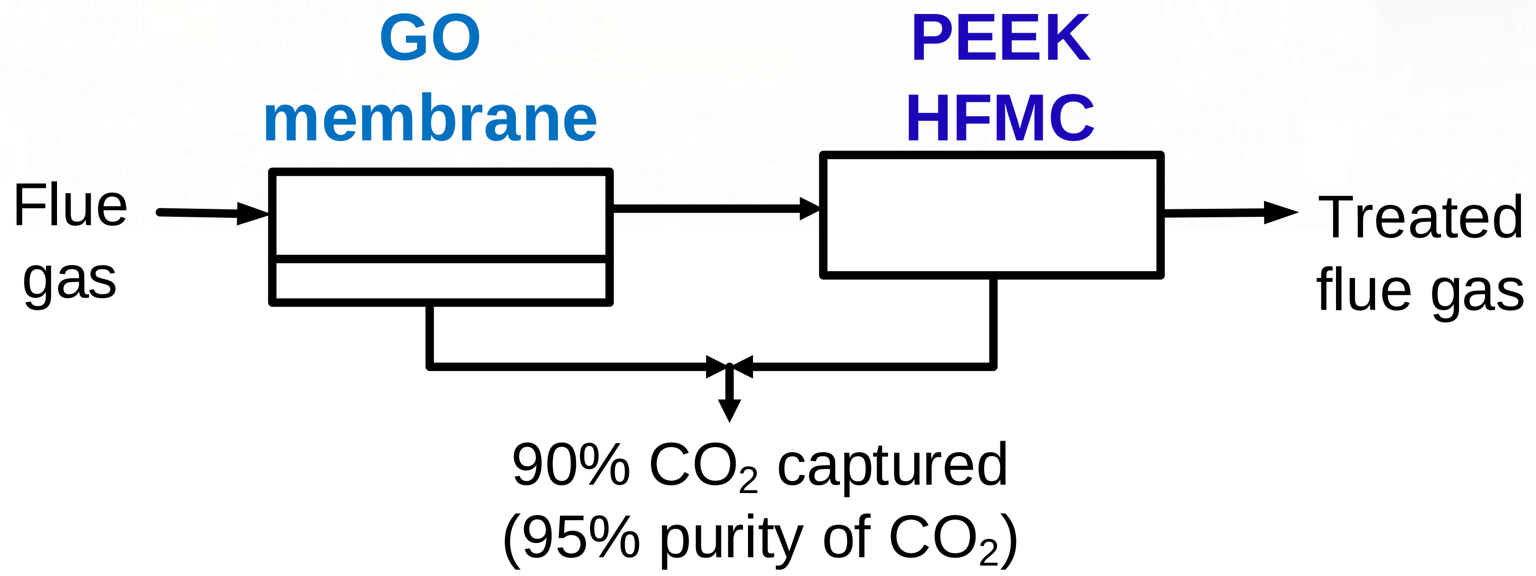
GO (graphene oxide): single-atomic layered, oxidized graphene

Science AAAS

Ultrathin, Molecular-Sieving Graphene Oxide Membranes for Selective Hydrogen Separation
Hang Li *et al.*
Science **342**, 95 (2013);
DOI: 10.1126/science.1236686

- **Objectives**: Develop a hybrid membrane process combining a graphene oxide (GO) gas separation membrane unit and a PEEK HFMC unit to capture ≥90% of the CO_2 from flue gases with 95% CO_2 purity
- **Team:** gti, Rensselaer, AIR LIQUIDE, ALaS, PoroGen, TRIMERIC CORPORATION

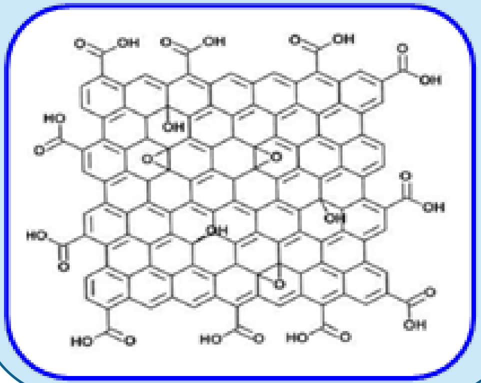
GO-HFMC process



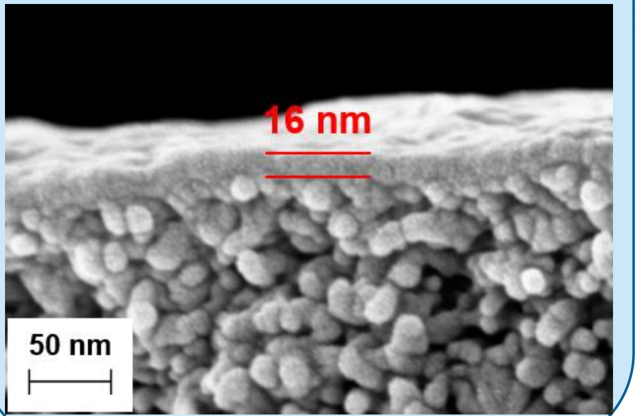
- GO-PEEK uses a conventional gas separation membrane unit to capture bulk of the CO_2 from flue gas followed by a PEEK HFMC unit to further capture CO_2 to achieve DOE's technical target
- GO membrane – CO_2 permeance ≥ 1,000 GPU – CO_2/N_2 selectivity ≥ 90
- HFMC – CO_2 permeance ≥ 3,000 GPU – CO_2 mass transfer coefficient ≥ 3 $(sec)^{-1}$

Advanced fabrication + unique GO properties → High performance CO_2 capture membrane

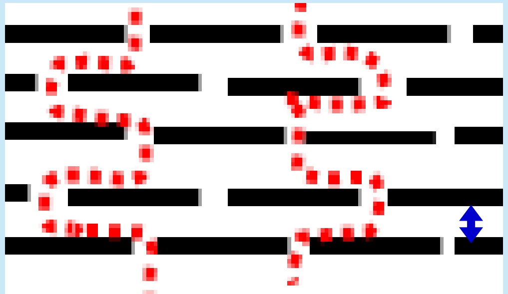
- GO: single-atomic layered, oxidized graphene



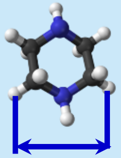
- Can be made ultra-thin, and thus high flux



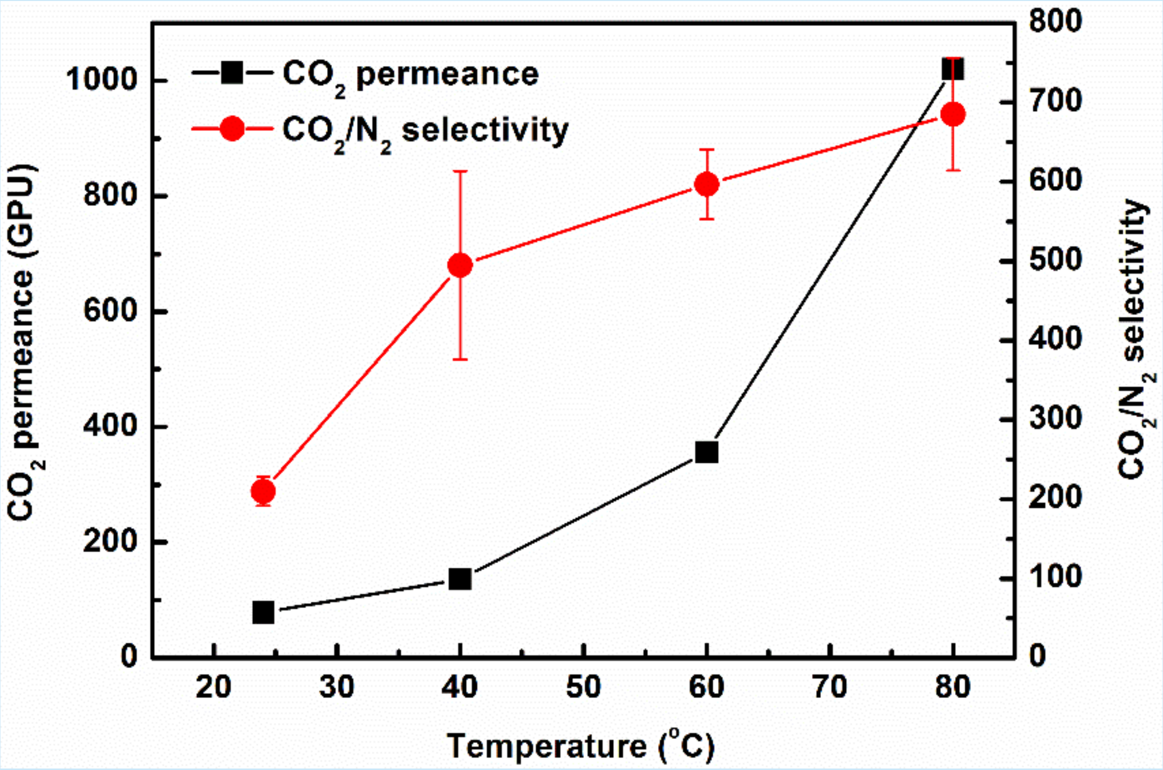
- Space in between GO layers filled with CO_2-philic agent, and thus high selectivity



CO_2-philic agent example: piperazine (PZ)



- High performance GO-PZ membrane



Feed: 15% CO_2/85%N_2 with saturated water vapor
Permeate: with sweep gas

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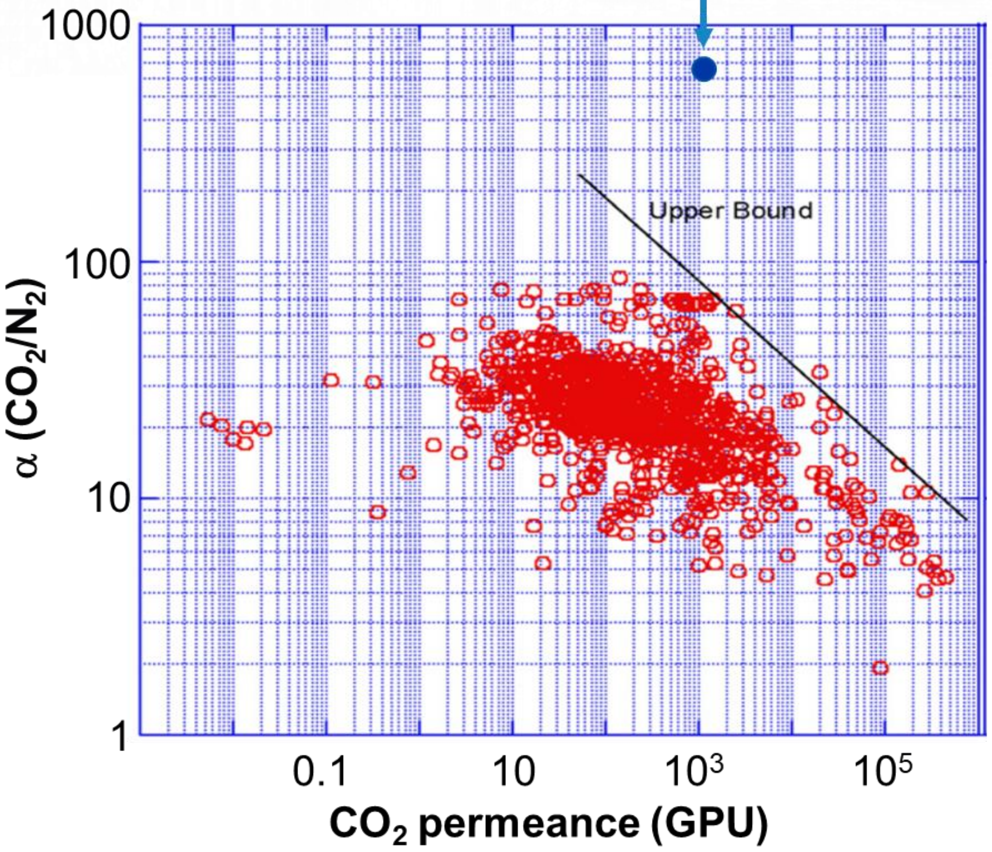
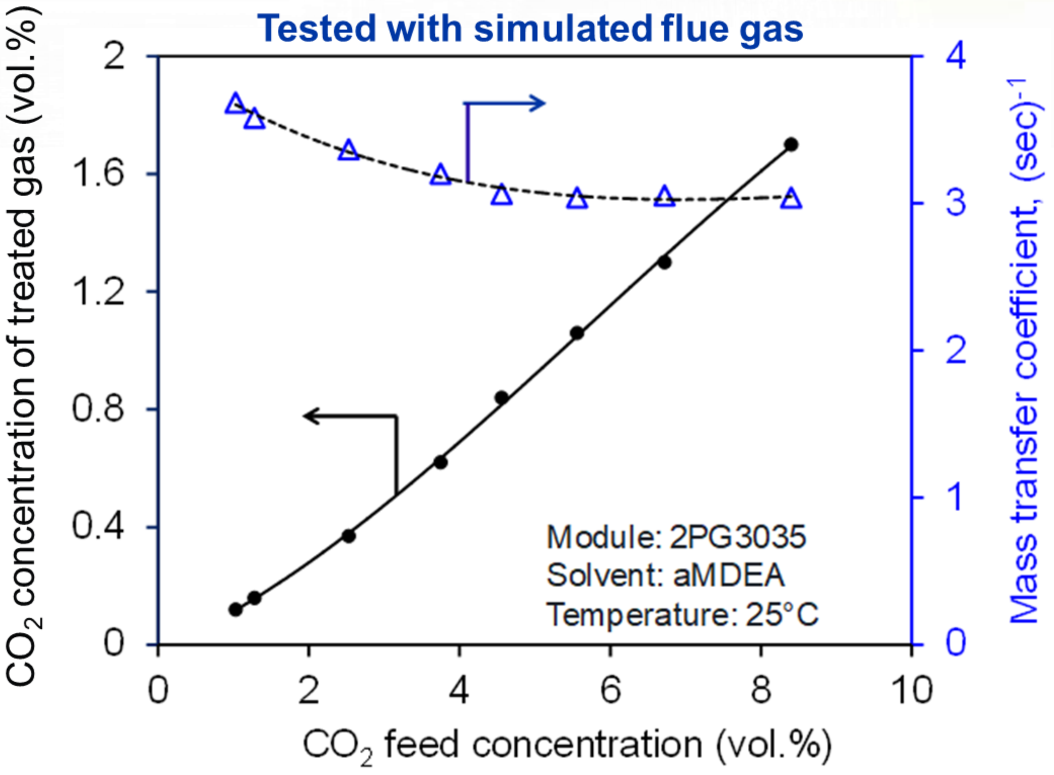
GO superior performance to polymeric membranes

Our GO membranes: P_{CO2}: 1000 GPU, α_{CO_2/N_2}: 680 (tested at 80°C with sweep gas)



PEEK HFMC effective for low CO_2-concentration feeds



Achieved goals of mass transfer coefficient > 3 $(sec)^{-1}$ and of permeance > 3000

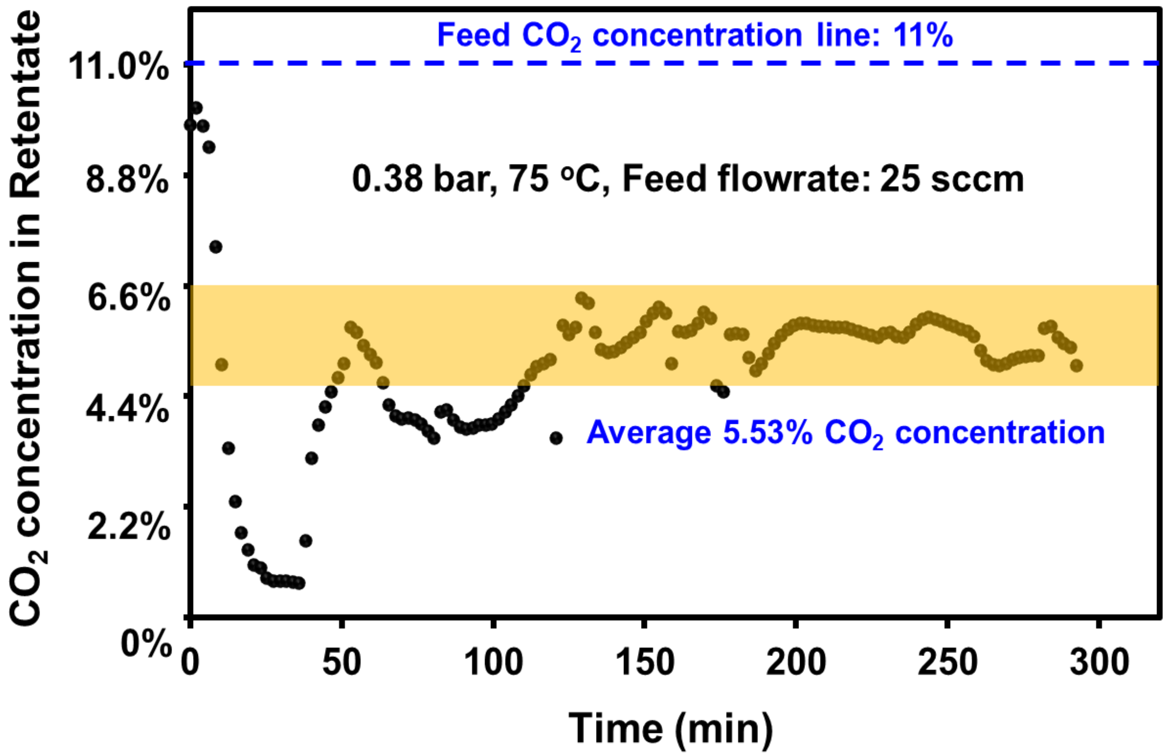
Robeson, J. Membrane Sci. ***2008****, Vol. 320, p390*

Note: Polymer data points (red): 100 nm membrane thickness assumed

Integrated testing ongoing, preliminary results indicated >90% CO_2 removal and >95% CO_2 purity

GO unit: Feed CO_2 concentration: 11 vol.%

- Retentate CO_2 concentration: 5.53 vol.%



PEEK unit: Feed CO_2 concentration: 5.53 vol.%

- Retentate CO_2 concentration: 0.21 vol.%
- CO_2 purity from regeneration: 96.9 vol.%

Component	Mol %	Det. Limit	Weight %
Helium		0.1%	
Hydrogen		0.1%	
Carbon Dioxide	96.9%	0.03%	97.9%
Oxygen/Argon	0.50%	0.03%	0.37%
Nitrogen	2.62%	0.03%	1.68%
Carbon Monoxide		0.03%	
Methane		0.002%	
Ethane		0.002%	
Ethene		0.002%	
Ethyne		0.002%	
Propane		0.002%	
Propene		0.002%	
Cyclopropane		0.002%	
Propadiene		0.002%	
Propyne		0.002%	
i-Butane		0.002%	
n-Butane		0.002%	
1-Butene		0.002%	
i-Butene		0.002%	
trans-2-Butene		0.002%	
cis-2-Butene		0.002%	
1,3-Butadiene		0.002%	
neo-Pentane		0.002%	
i-Pentane		0.002%	
n-Pentane		0.002%	
Pentenes		0.002%	
Hexane Plus		0.002%	
Hydrogen Sulfide		0.10%	
Total	**100.0%**		**100.0%**

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3rd Generation Technology: GO^2 Process

nature COMMUNICATIONS

ARTICLE

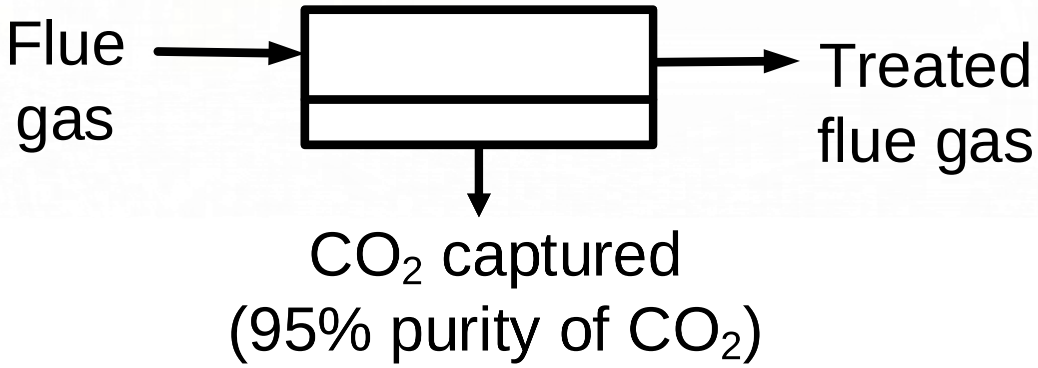
DOI: 10.1038/s41467-017-02318-1 OPEN

Ultrathin graphene oxide-based hollow fiber membranes with brush-like CO_2-philic agent for highly efficient CO_2 capture

Fanglei Zhou[1], Huynh Ngoc Tien[2], Weiwei L Xu[2], Jung-Tsai Chen[2], Qiuli Liu[2], Ethan Hicks[2], Mahdi Fathizadeh[2], Shiguang Li[3] & Miao Yu[1]

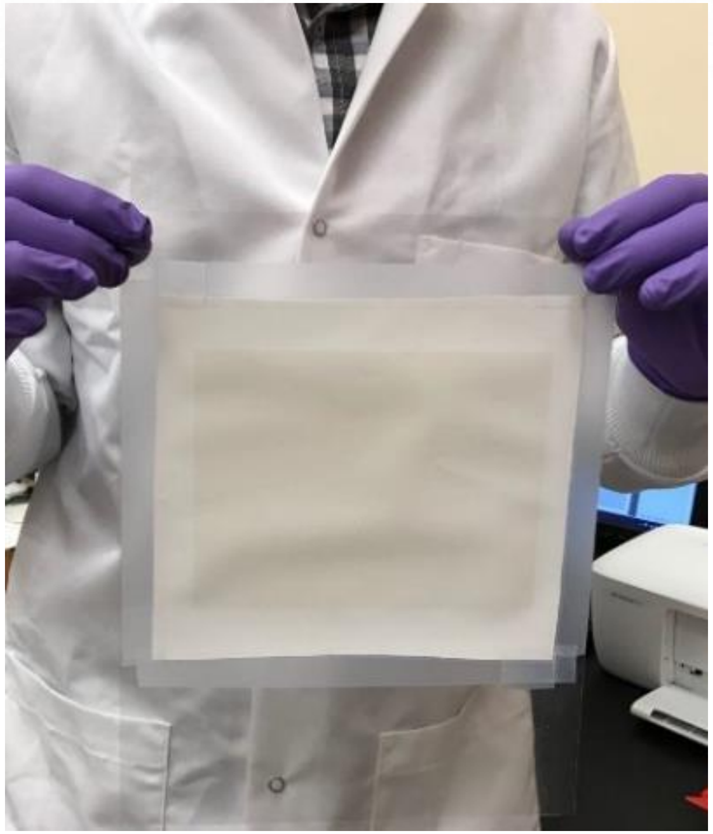
- **Objective**: Develop a transformational graphene oxide (GO)-based membrane process (**GO^2**) for CO_2 capture with 95% CO_2 purity
- **Team:** gti Rensselaer THE OHIO STATE UNIVERSITY TRIMERIC CORPORATION NATIONAL CARBON CAPTURE CENTER

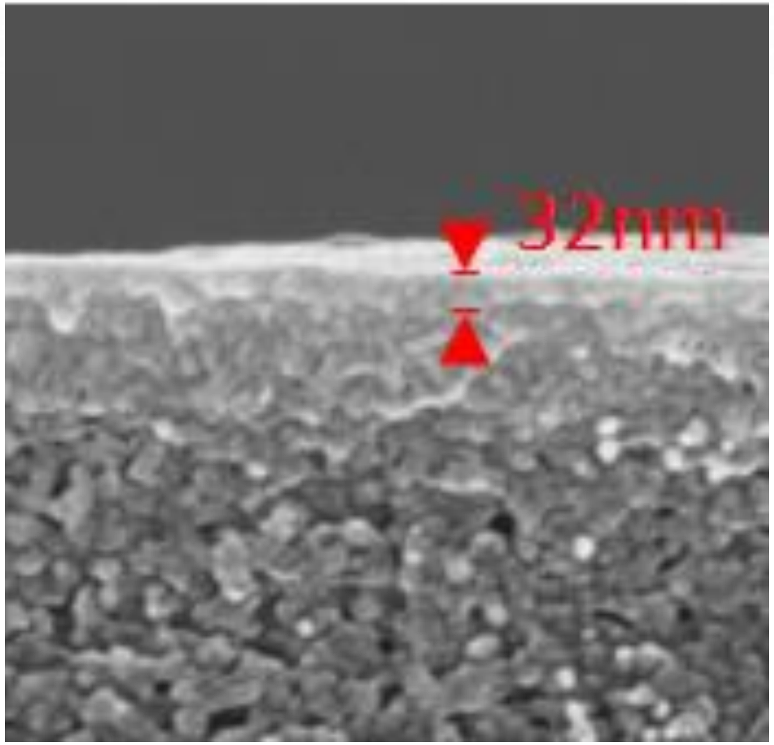
Process description

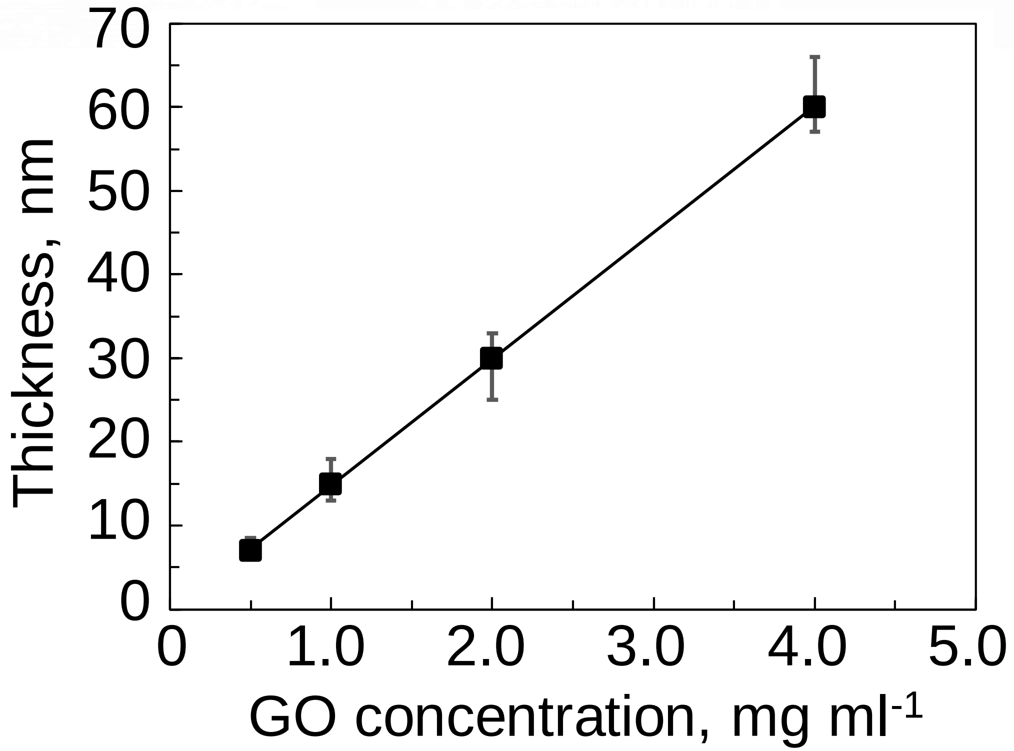


- 90% removal from coal or natural gas flue gases: a proprietary **GO² process** integrates a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for optimal performance
- GO-1: selectivity ≥200 and CO_2 permeance ≥1,000 GPU
- GO-2: selectivity ≥ 20 and CO_2 permeance ≥2,500 GPU

In addition to hollow fiber membranes, flat sheet membranes were successfully prepared by printing

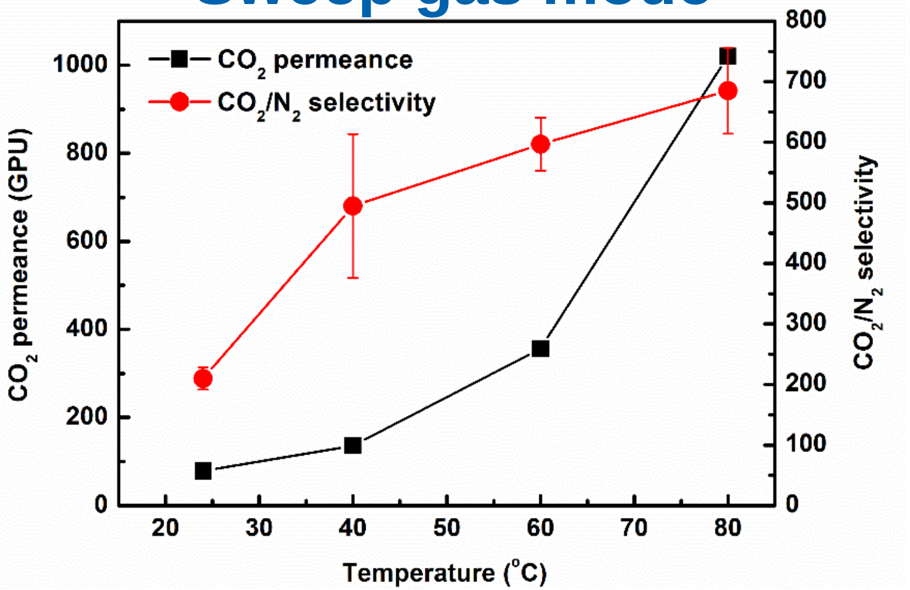






GO-1 membrane: 1,000 GPU CO_2 permeance with selectivity >600

Sweep gas mode

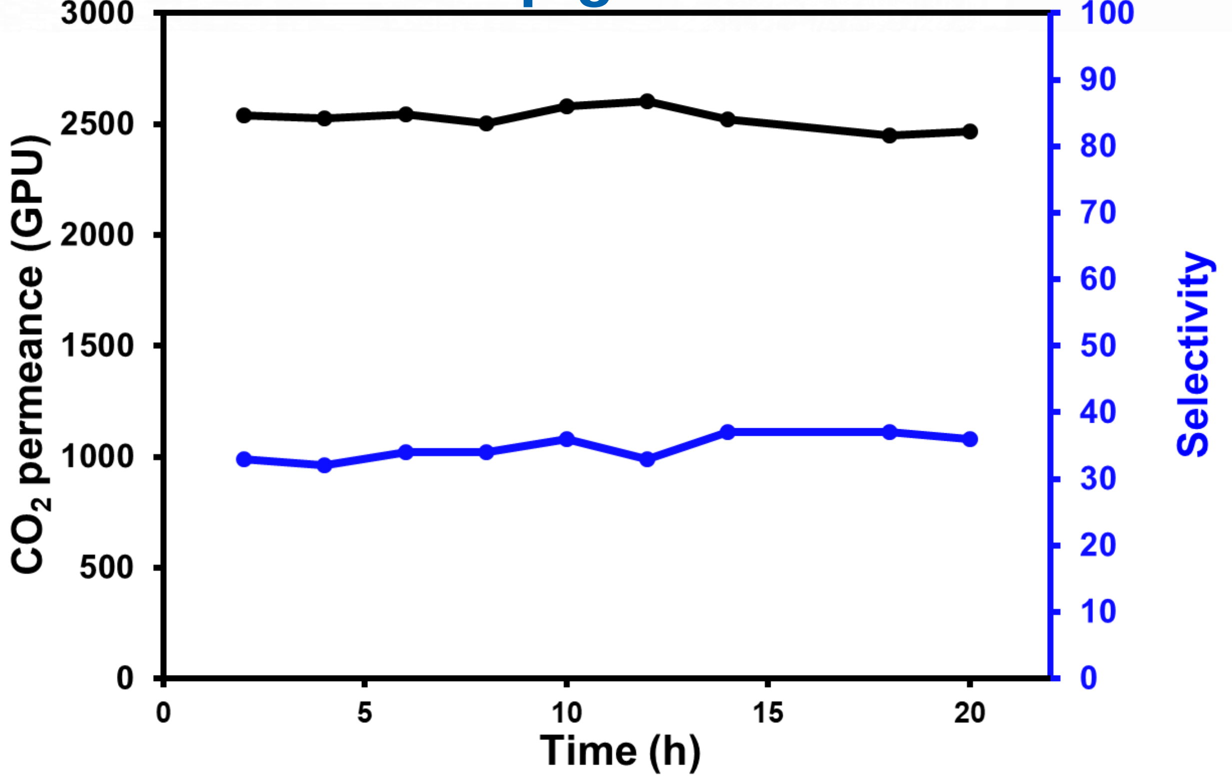


Vacuum mode

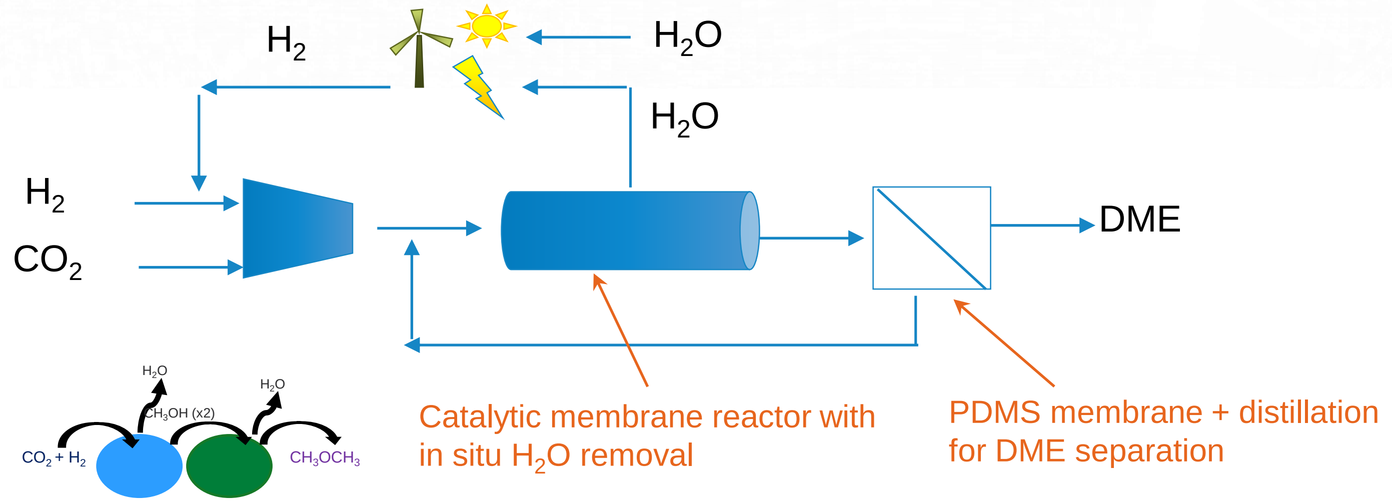
Temperature	75 °C
CO_2 permeance, GPU	**1080 ± 55**
CO_2/N_2 selectivity	**650 ± 31**

GO-2 membrane: 2,500 GPU CO_2 permeance with selectivity >30

Sweep gas mode



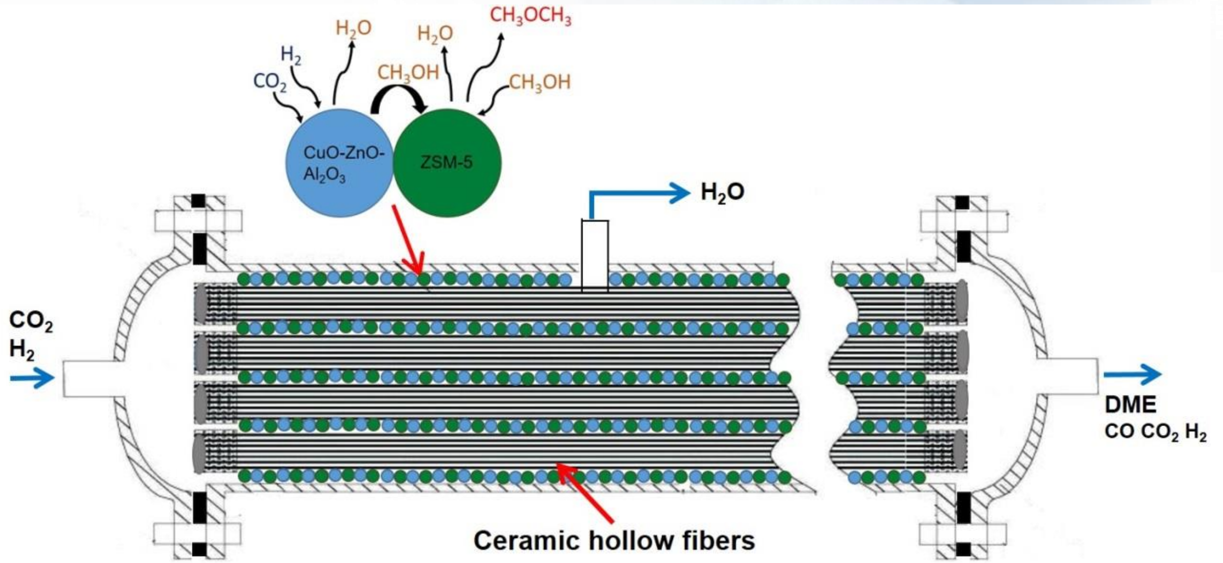
Membrane Reactor for DME Production



- **Objectives**: Demonstrate production of DME on a 1 kg/day scale from CO_2 and H_2 using a novel catalytic membrane reactor. Perform a market analysis and TEA to achieve a target SUE of 0.254 $/kWh DME.
- **Team:** gti, Missouri S&T University of Science & Technology, Rensselaer

New approach to making DME

- Feed H_2 and CO_2 not CH_4 and H_2O
- Bifunctional catalyst and membrane reactor shift equilibrium towards product formation
- Membrane removes produced water in situ
  - improves catalyst stability
  - shifts equilibrium to higher CO_2 conversion and DME yields
- Compact, modular design
- Lower production cost
- Seeking commercialization partners

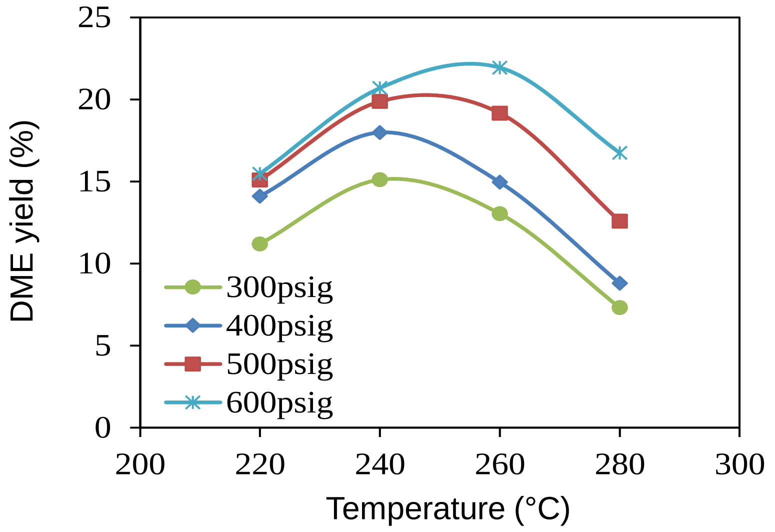


Membrane reactor at 200-300 °C and pressures up to 500 psi

1. **Methanol synthesis**: $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
2. **DME synthesis**: $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$

Overall reaction: $2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + \mathbf{3H_2O}$

Bi-functional catalyst performance

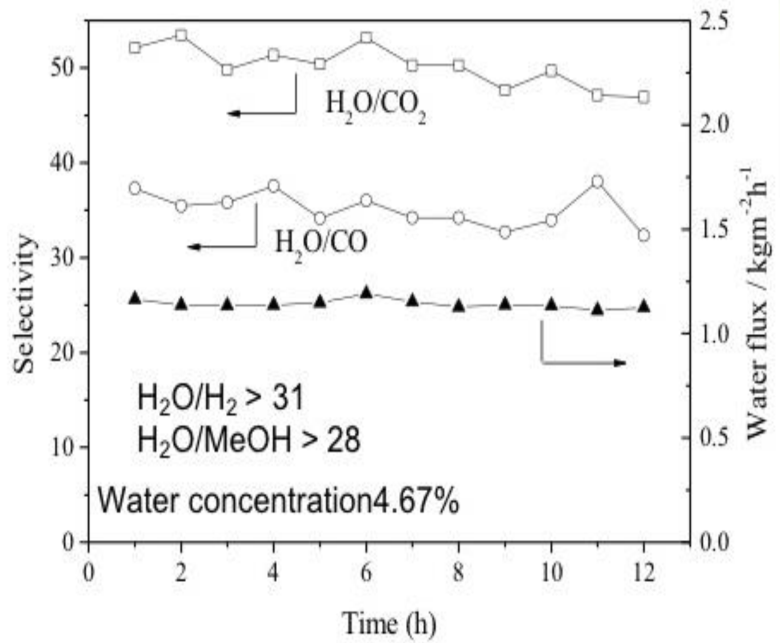


- Catalyst achieved DME yield of 22%

Catalyst Properties

- Methanol synthesis: $CuO/ZnO/Al_2O_3$
- DME synthesis: H-ZSM-5
- BET surface area 132 m^2/g
- Particle size 10-30 nm

Water-selective membrane performance

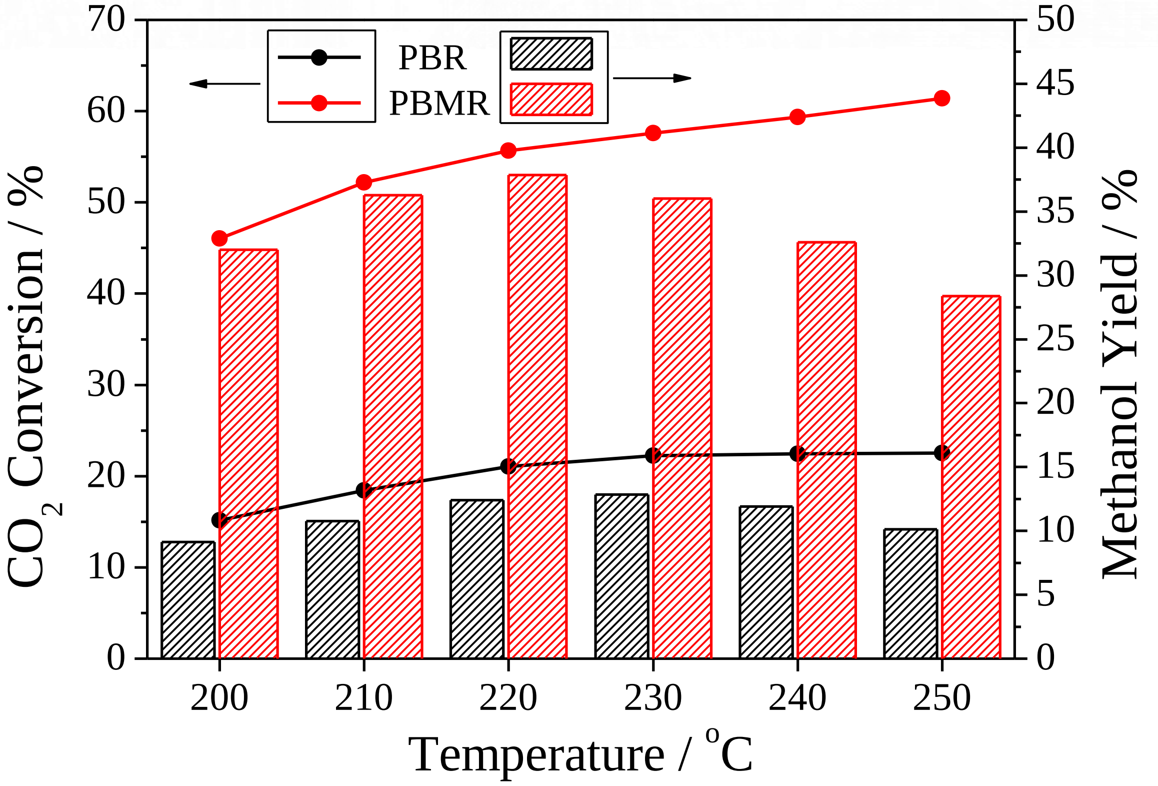


Membrane Properties

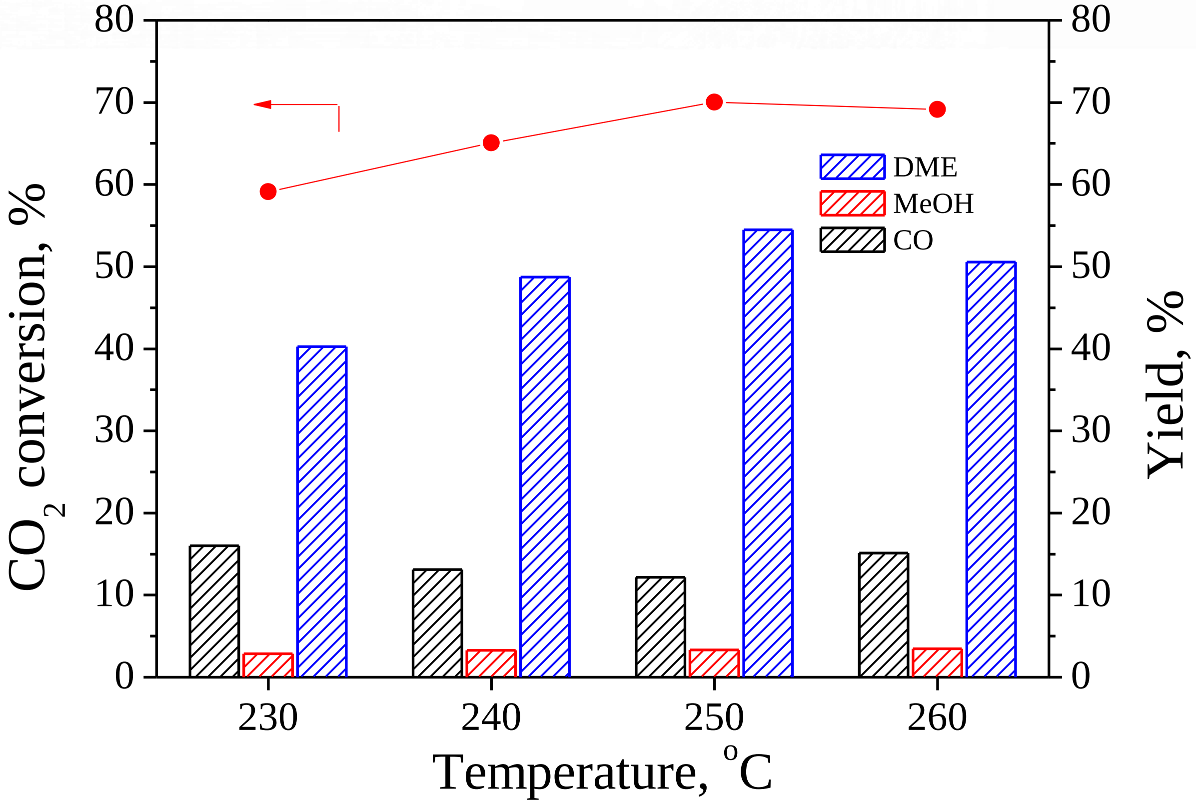
- Uniform membrane; no pinholes or cracks
- Selectivity >30 for H_2O over CO_2, CO, H_2, MeOH at 200 °C, 300 psig

Typical impact of the membrane reactor on methanol and DME production compared with packed-bed reactor

Pressure: 500 psig



Pressure: 500 psig



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CO_2 Capture Project - Phase 4

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ALaS

For additional information contact Howard Meyer (hmeyer@gti.energy)

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