Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

primary project goals

Arizona State University's (ASU) project objectives are to develop tools and methods for scaling-up zeolite membrane fabrication and water-gas shift (WGS) zeolite membrane reactors (ZMRs), and to construct bench-scale zeolite membrane modules and test their performance for WGS with carbon dioxide (CO_2) capture on coal-derived syngas.

This will be the first effort to study ZMRs for high-temperature chemical reaction and gas separation at this scale. The process design and techno-economic analysis (TEA), with the input of the experimental findings, will validate the effectiveness of the ZMR for WGS reaction and CO_2/hydrogen (H_2) separation. The results of this project will provide a foundation and guide for further scaling-up of the membrane reactor technology for pre-combustion CO_2 capture at pilot-scale.

technical goals

- Identify structure and operation conditions for a bench-scale membrane reactor through modeling and experimental study of the WGS reaction in a single-tube ZMR.
- Fabricate chemically and thermally stable alumina tubule supports and zeolite membranes of suitable quantity in consistent quality.
- Design and fabricate multiple-tube zeolite membrane modules with adequate seals for H_2 separation and WGS reaction at high temperature and pressures.
- Assemble and test the bench-scale zeolite membrane modules with desired catalyst for WGS reaction.
- Demonstrate effective production of H_2 and CO_2 capture by the bench-scale ZMR from coal gasification syngas at temperatures of 400 to 550°C and pressures of 20 to 30 atmosphere (atm), to produce 2 kg H_2/day (equivalent to 2 kilowatt-thermal [kW_{th}] integrated gasification combined cycle [IGCC] power plant).
- Perform process design and techno-economic and environmental, health, and safety (EH&S) risk analyses to evaluate performance and cost-effectiveness of the ZMR integrated in a 550-megawatt-electric (MW_e) IGCC plant with CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced, in whole, by a novel WGS shift reactor that integrates zeolite-based H_2 separation membranes. Within the zeolite membrane WGS reactor, H_2 would be withdrawn directly from the reaction chamber, efficiently increasing the driving force for the WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are

technology maturity:
Bench-Scale, Actual Syngas (2 kg per day equivalent to 2 kWth)

project focus:
Zeolite Membrane Reactor

participant:
Arizona State University

project number:
FE0026435

predecessor projects:
N/A

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partners:
Media and Processes Technology Inc., University of Cincinnati, Nexant Inc.

start date:
10.01.2015

percent complete:
95%

replaced by a single, elegantly performing reactor. This process concept, with the ZMR replacing the conventional WGS process stages and amine absorption unit, is depicted in Figure 1.

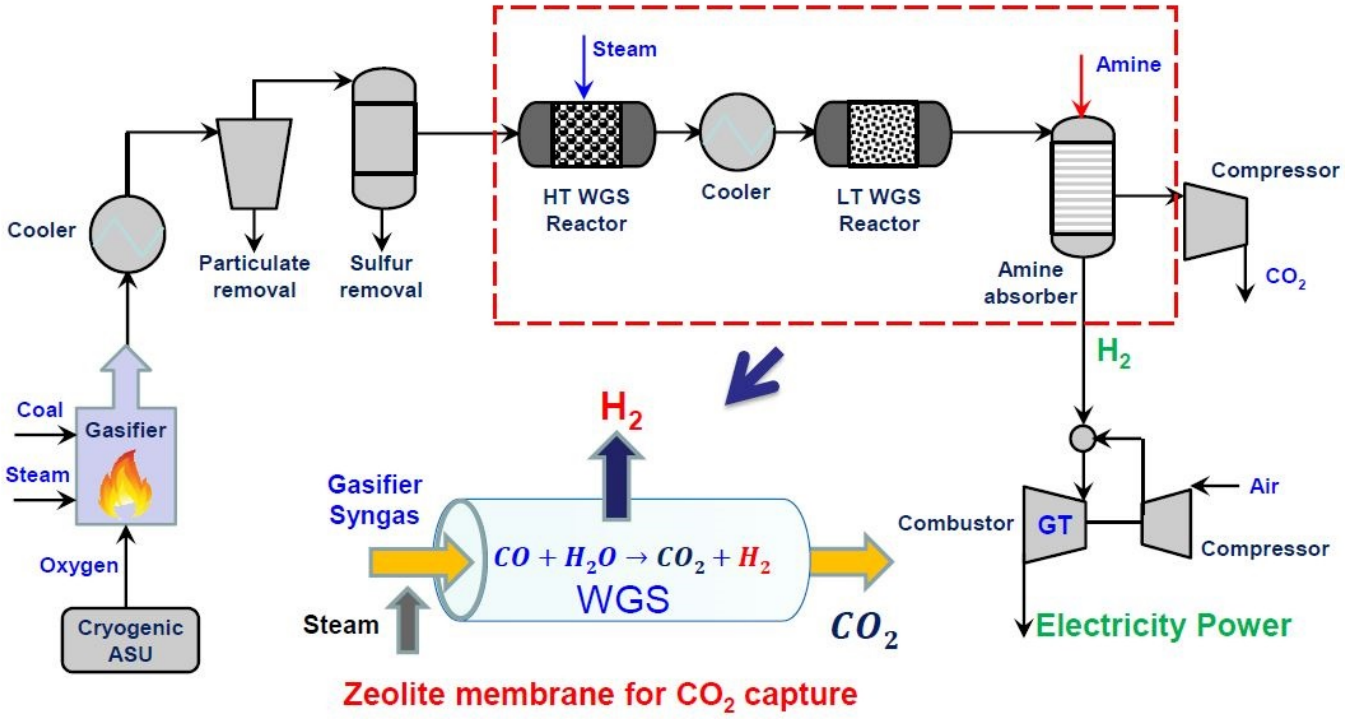

Figure 1: Zeolite membrane reactor for WGS reaction and CO_2 capture in context of coal gasification plant cycle.

However, the operating environment in the reactor is challenging. Past findings have suggested that zeolite membranes, which are inorganic and can be tailored or selected for specific gas-separation applications, can meet the functional requirements and operational conditions as follows:

- Operation at 350 to 550°C.
- Chemically stable in hydrogen sulfide (H_2S), thermally stable at ≈400°C.
- Hydrogen permeance = 2×10^{-7} mol/m^2.s.Pa (600 GPU).
- Hydrogen/CO_2 selectivity = 20 to 40.

In ASU's previous work, Mobil-type 5 (MFI) zeolite (an aluminosilicate zeolite belonging to the pentasil family of zeolites) was used in a laboratory-scale zeolite membrane WGS reactor and continues as the basis in current work. See Figure 2 for the zeolite structure and a highly magnified view of the zeolite layer deposited on an alumina substrate. Although this zeolite has been traditionally used as a catalyst for hydrocarbon isomerization and the alkylation of hydrocarbons, it serves in the current work as an H_2-permeable membrane layer suitable for deposition on alumina, which can be formed into the desired tubes for fitting into WGS reactor modules.

The MFI zeolite pores have an effective diameter of ~0.56 nm, which is large enough for the small gas molecules involved in the WGS reaction to permeate through by gaseous diffusion mechanism. Therefore, pristine MFI-type zeolite membranes offer high H_2 permeance but with limited H_2/CO_2 selectivity defined by the Knudsen factor (~4.75) at high temperatures where the permeating gases become non-adsorbing to the zeolite. The MFI-type zeolite membranes can be modified by in situ deposition of mono silica species to the internal pore wall that narrows down the effective zeolite pore diameter from ~0.56 nm to less than 0.36 nm. Such a reduced pore size enables the highly selective size-exclusion effect between the small H_2 molecule (kinetic diameter d_k = 0.289 nm) and other slightly larger molecules like CO_2 (d_k = 0.330 nm), carbon monoxide (CO) (d_k = 0.376 nm), and methane (CH_4) (d_k = 0.380 nm).

ASU and the University of Cincinnati have developed an on-stream catalytic cracking deposition (CCD) method for modification of the MFI-type zeolite membrane that effectively controls the silica deposition within a small portion of the zeolitic channels near the membrane surface. This well-controlled modification avoids excessive loss in H_2 permeance while achieving substantially improved H_2 selectivity over CO_2, CO, and water (H_2O).

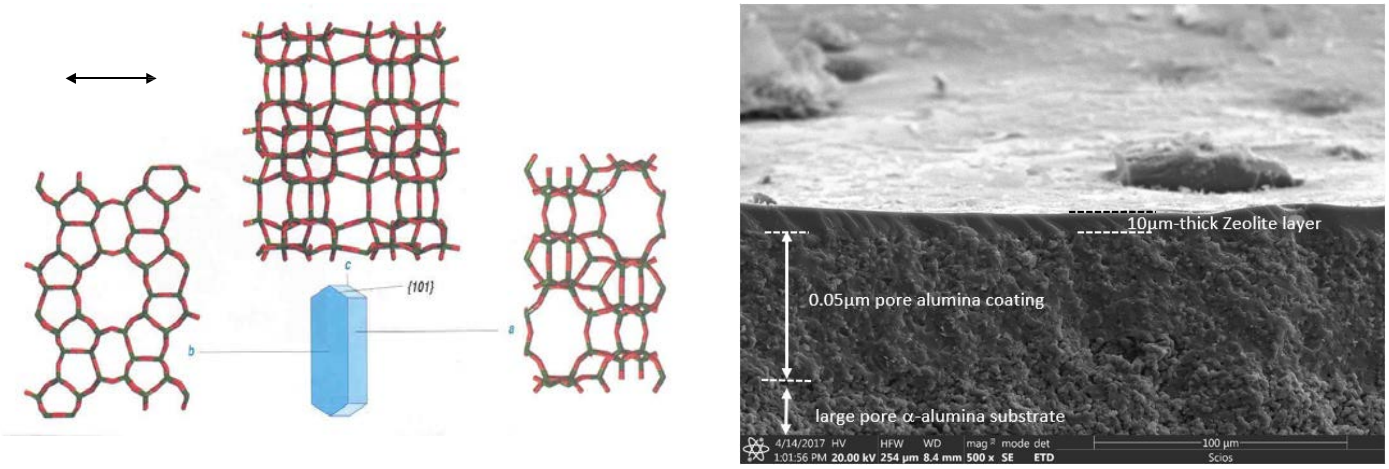

Figure 2: MFI-type zeolite (ZSM-5 or silicalite) (on left); magnified view of zeolite membrane (on right).

Figure 3 depicts the laboratory-scale tubular membrane reactor for testing separation performance and WGS reaction of a zeolite membrane tube containing a WGS catalyst. Feed gas is passed to the bore side of the tube, and as the gas passes over the catalyst, increasing amounts of H_2 are generated. The zeolite allows H_2 to readily pass through the membrane tube, while keeping the larger CO, H_2O, and CO_2 molecules inside. Retentate is enriched in CO_2 after the WGS reaction.

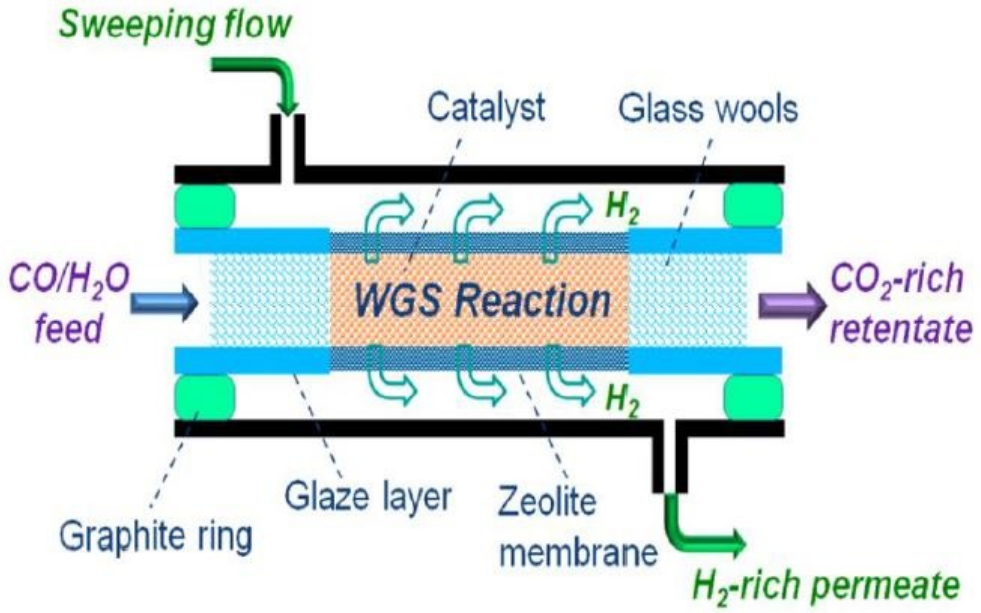

Figure 3: Zeolite membrane tubular WGS reactor.

Previously, CCD-modified MFI zeolite membranes showed long-term stability in WGS reaction at 400 to 550°C with a high H_2S content of ~400 parts per million (ppm) in feed. Modified MFI zeolite membranes with an H_2/CO_2 selectivity higher than 10 showed the ability to achieve CO-conversion well exceeding the equilibrium conversion in WGS reaction.

In this project, ASU reported the first experimental demonstration of near-complete CO conversion (~99.9%) in a single high-temperature and high-pressure WGS-ZMR that uses a CCD-modified MFI zeolite membrane supported on a commercially available low-cost small diameter alumina tube (outer diameter: 5.7 mm, provided by Media and Processes Technology Inc.).

This basic arrangement persists in the multi-tube reactors for bench-scale testing (these modules are depicted in Figure 4). The housing accommodates a full-length, 21-tube bundle, and the main feed port can be completely removed to permit catalyst packing/removal.

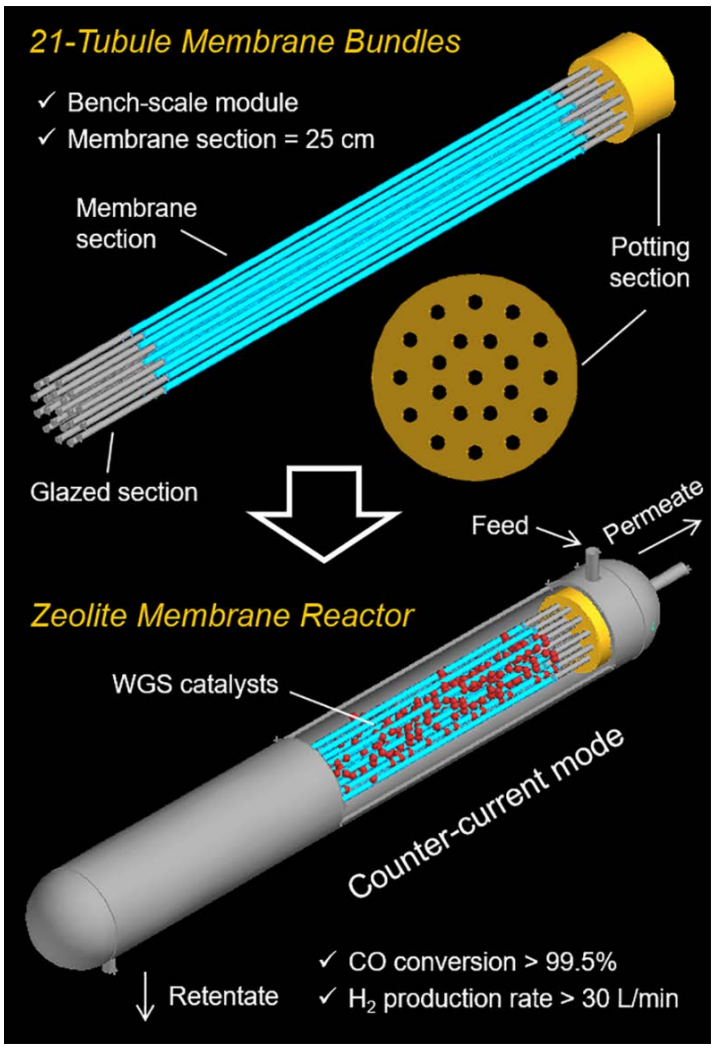

Figure 4: Zeolite membrane bundles and modules.

ASU performed a 425-hour challenge test on the 21-tube ZMR bundle and seals to evaluate performance and durability. Testing conditions were at temperatures from 400 to 450°C, pressure from 100 to 400 pounds per square inch (psi), and steam content from 60 to 100%. No deterioration was noted throughout the duration of the testing, as depicted in Figure 5.

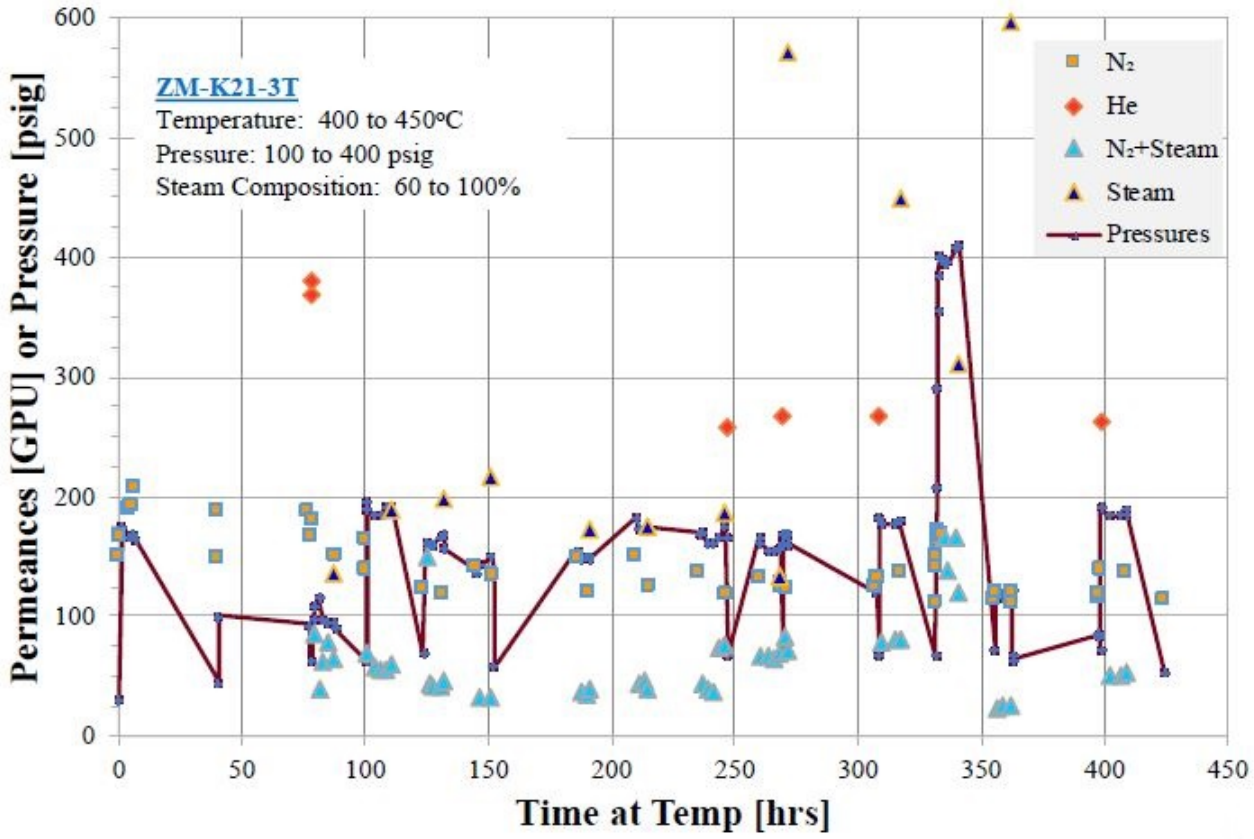

Figure 5: Challenge testing on zeolite tube bundles.

ASU completed fabrication and installation of the bench-scale reactor test skid at the University of Kentucky facility, and testing is underway.

Preliminary performance results of the WGS-ZMR have been used in process modeling and a TEA of a ZMR-based IGCC plant scenario; the results were compared to a National Energy Technology Laboratory (NETL) baseline case (conventional WGS and Selexol acid gas removal [AGR]) and the Nexant IGCC case. Compared to the NETL baseline, which has a cost of electricity (COE) of 141.5 mills/kilowatt-hour (kWh), including CO_2 transportation, storage, and monitoring (TS&M), the ZMR COE was higher at 147.3 mills/kWh. Notwithstanding somewhat lower capital costs, auxiliary power consumption is higher in the ZMR case, chiefly causing the higher COE.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value *	Target R&D Value
Materials of Fabrication for Selective Layer	—	modified MFI zeolite	modified MFI zeolite
Materials of Fabrication for Support Layer	—	α-alumina	α-alumina
Nominal Thickness of Selective Layer	μm	~10	~5
Membrane Geometry	—	discs	tubes
Maximum Trans-Membrane Pressure	bar	~20	~30
Hours Tested without Significant Degradation	—	~100	>200
Manufacturing Cost for Membrane Material	$/m^2	~800	~600
Membrane Performance			
Temperature	°C	400-500	400-500
H_2 Pressure Normalized Flux	GPU or equivalent	~300	300-600
H_2/H_2O Selectivity	—	>100	>100
H_2/CO_2 Selectivity	—	10–30	20-45
H_2/H_2S Selectivity	—	>60	>60
Sulfur Tolerance	ppm	1,000	10,000
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	Counter-current	
Packing Density	m^2/m^3	50-200	
Shell-Side Fluid	—	Retentate, CO_2-rich flow	
Syngas Gas Flowrate	kg/hr	5-20	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	95 **	~30
H_2 Recovery, Purity, and Pressure	%/%/bar	92	95	~20
Pressure Drops Shell/Tube Side	bar	10-30	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	~1,000	

* For the Current R&D Value, the calculation is based on lab-scale zeolite membranes reported in literature. Palladium-based membranes have high hydrogen selectivity but low sulfur tolerance, which is not presented here.
** Gasifier, coal feedstock, and upstream unit operation (e.g., syngas pretreatment) specifications dependent.

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 mercury (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; target permeance and selectivity 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 cocurrent, countercurrent, crossflow 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.

Other Parameter Descriptions:

Membrane Permeation Mechanism – At temperatures above 400°C, the separation of H_2 and CO_2 through modified zeolite membranes is governed by translational gas diffusion in micropores.

Contaminant Resistance – Zeolite membranes and catalysts have excellent resistance to syngas contaminants.

Syngas Pretreatment Requirements – Particulate removal is required.

Membrane Replacement Requirements – The multiple-tube membrane bundle will be applied in the ZMR continuously over 200 hours without replacement.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere. For example, the condensed water at the outlet of retentate side is recycled back as makeup water for the WGS reaction.

Process Design Concept – As presented in Figure 1. A skid for bench-scale ZMRs consisting primarily of a flow control system and a high-temperature oven is connected into a coal-to-liquids facility by replacing the WGS unit.

Proposed Module Integration – The proposed bench-scale study of ZMRs will be conducted at the University of Kentucky, Center for Applied Energy Research. The multiple-tube membrane bundle will be located downstream of a Coal/Biomass-to-Liquids (CBTL) pilot facility that produces syngas with a rated feed capacity of 1 ton/day. The pressure and temperature of syngas entering the membrane module are 435 pounds per square inch absolute (psia) and 845°F, respectively. The composition of the gas mixture is assumed:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435	845	32.3	34.1	0	2.8	25.7	3.4	>400

technology advantages

- The membrane reactor process could replace a conventional two-stage WGS reactor system requiring intercooling and a separate CO_2 capture unit, with a single WGS membrane reactor unit with potential for energy efficiency increase and equipment cost savings.
- Modified MFI zeolite membranes have remarkable resistance to sulfur species in the syngas feed and good thermal and hydrothermal stability and show superior hydrogen permeance and high H_2/CO_2 selectivity.
- These tubular membranes can be fabricated into robust and stable multiple-tube modules at a high packing density.
- The ZMR-based process will create a high-pressure CO_2 stream, capturing greater than 90% of CO_2 in post-shift syngas.

R&D challenges

- Low reproducibility of laboratory fabrication of long-tube zeolite membranes in large quantity with H_2 separation performance the same as a single, short-tube membrane.
- High-temperature hydrothermal stability of membrane bundle components and seals.
- Deterioration of strength of membrane tubes in use.
- WGS catalysts' thermal stability, poison resistance, and product selectivity maintained at high pressures (greater than 15 atm) and temperatures (up to 550°C).
- Removal of particulate matter from the syngas to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials if the technology is to become economically viable.

status

Zeolite membranes have been fabricated on cost-effective industrial tubular alumina substrates, and high-pressure and high-temperature intermediate-scale zeolite membrane modules have been built and tested. WGS on ZMR was studied by experiments and modeling. Also, a process concept for ZMR integration into an IGCC power plant system has been identified and will serve as the basis for eventual cost and performance estimates for this technology.

available reports/technical papers/presentations

"*Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Jerry Lin, Arizona State University, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, Pittsburgh, PA, August 2019.

"*Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture*," MPT Site Visit, February 2019.

"*Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Lie Meng, Arizona State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

A. Arvanitis, X. Sun, S. Yang, D. Damma, P. Smirniotis, J. Dong, "*Approaching complete CO conversion and total H_2 recovery for water gas shift reaction in a high-temperature and high-pressure zeolite membrane reactor*," Journal of Membrane Science, 549 (2018) 575–580.

"*Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Jerry Lin, Arizona State University, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture*," presented by Jerry Lin, Arizona State University, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.