Integrated Multichannel Water-Gas Shift Catalytic Membrane Reactor for Pre-Combustion Carbon Capture

primary project goal

The Bettergy Corporation team has been developing an integrated catalytic membrane reactor (CMR) system that combines, in a one-stage process, a high-temperature water-gas shift (WGS) reaction with a hydrogen (H_2) separation membrane to produce H_2 while simultaneously delivering carbon dioxide (CO_2) at high pressure, minimizing the cost of CO_2 compression. The novel process depends on a robust modularized membrane supported on catalytic substrates, which is based on Bettergy's patented nanopore engineering membrane platform technology. Previously, a lab-scale WGS-CMR system was successfully tested, achieving high WGS conversion, high-purity H_2 through membrane separation, and enriched CO_2 in the retentate stream. Currently, the main project goals are to optimize the process, develop and test a multichannel prototype system, and generate a commercialization plan.

technical goals

- Optimize the formulation for the catalytic membrane substrate.
- Develop and optimize the fabrication processes for making both tubular and multichannel membrane substrates.
- Optimize membrane synthesis procedures on the substrates.
- Optimize CMR performance to attain carbon monoxide (CO) conversion exceeding the thermodynamic limit at high temperature (up to 500°C) and pressure of 450 pounds per square inch (psi).
- Investigate the effect of impurities (e.g., hydrogen sulfide [H_2S]) on membrane performance, and achieve stability of at least 500 hours without appreciable degradation.
- Demonstrate prototype performance at syngas (simulated) flow rate of 5 kg/day.
- Enable improvement of energy efficiency of a WGS-CMR system integrated in a 550-megawatt-electric (MWe) integrated gasification combined cycle (IGCC) plant with CO_2 capture by 25 to 30%, relative to a multistage WGS reaction with amine-based carbon capture and pressure swing adsorption (PSA) H_2 purification.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification or steam reforming 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 one-stage WGS-CMR process unit. In this one-stage process, the WGS reaction occurs in the CMR, which incorporates H_2 separation membranes that permit pure H_2 to be drawn off, efficiently increasing the driving force for the equilibrium WGS reaction to go to completion. Carbon dioxide exiting the WGS-CMR

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Water-Gas Shift Catalytic Membrane Reactor

participant:
Bettergy Corporation

project number:
SC0018853

predecessor projects:
N/A

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partners:
University of Cincinnati; Dawnbreaker Inc.

start date:
07.02.2018

percent complete:
85%

remains at relatively high pressure, reducing subsequent CO_2 compression costs. As a result, the multiple stages of the conventional WGS unit would be replaced by a single-stage reactor (or banks of reactors in parallel as syngas throughput requires). The process concept is depicted in Figure 1 (for a natural gas reforming scenario).

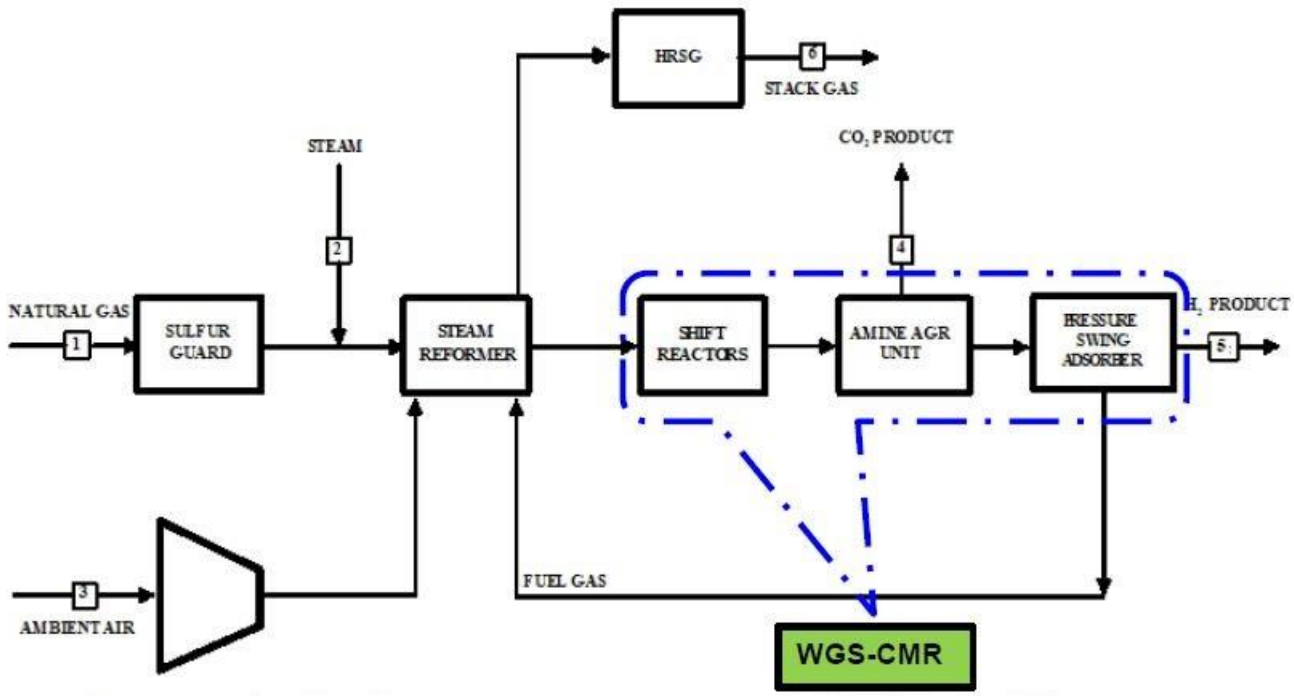

Figure 1: WGS-CMR (in green shadow) replacing two-stage shift, amine CO_2 capture, and PSA systems (in blue envelope) in natural gas steam reforming H_2 production process.

The basic structure of the WGS-CMR consists of tubular channels having a configuration of the sort illustrated in Figure 2. Each reactor gas channel consists of a porous tubular support on which two different active layers are applied. The internal tube layer is made of WGS catalyst, while the outer layer is an H_2-selective zeolite. Pressurized syngas flows through the bores of the tubes, where it contacts the WGS catalyst layer inducing increased H_2 production. The H_2 permeates through the support and can exit through the outside selective layer. Other syngas species do not readily permeate through the outside zeolite layer and remain at pressure inside the tubes. Given suitable WGS kinetics and gas flow rates, high levels of syngas conversion can be obtained, and a large fraction of H_2 can be recovered on the permeate side of the reactor. Retentate from the reactor can be made to contain most of the carbon in the incoming syngas in the form of CO_2. An alternate WGS-CMR configuration is similar but dispenses with the WGS layer and has only an H_2-selective layer on a porous substrate of WGS catalyst. In this case, the WGS catalyst may be in monolith form with many channels, with the H_2-selective zeolite layer on the outside surface of the monolith.

The dimensions of the gas channels may be made very small, and as such the WGS-CMR is a type of microchannel membrane reactor. Microchannel reactors offer multiple benefits, including better control over temperature profiles, minimal catalyst loading for given levels of gas throughput, moderate pressure drop, and favorable trade-off between capital cost and performance.

This novel WGS-CMR does pose developmental challenges, including optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate), preparing the H_2-selective composite zeolite thin layer membrane on the support/substrate, and development and optimization of WGS-CMR assemblies.

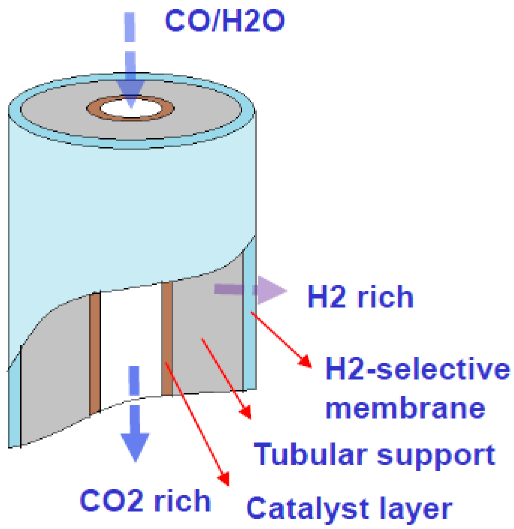

Figure 2: WGS-CMR tubular configuration.

One closely investigated configuration is a catalytic tubular substrate (CTS), which consists of WGS catalyst incorporated into the tubular support itself. A mixture of alumina and WGS catalyst powder (FeCr), plus binders/additives, has been extruded in single-channel tubes and sintered/heat treated (see Figure 3). This process has been optimized, resulting in CTSs with 1-inch diameter reliably prepared and reaching a length of 30 cm free of cracks. These include a surface modification technique for zeolite seed layer coating and membrane in situ growth.

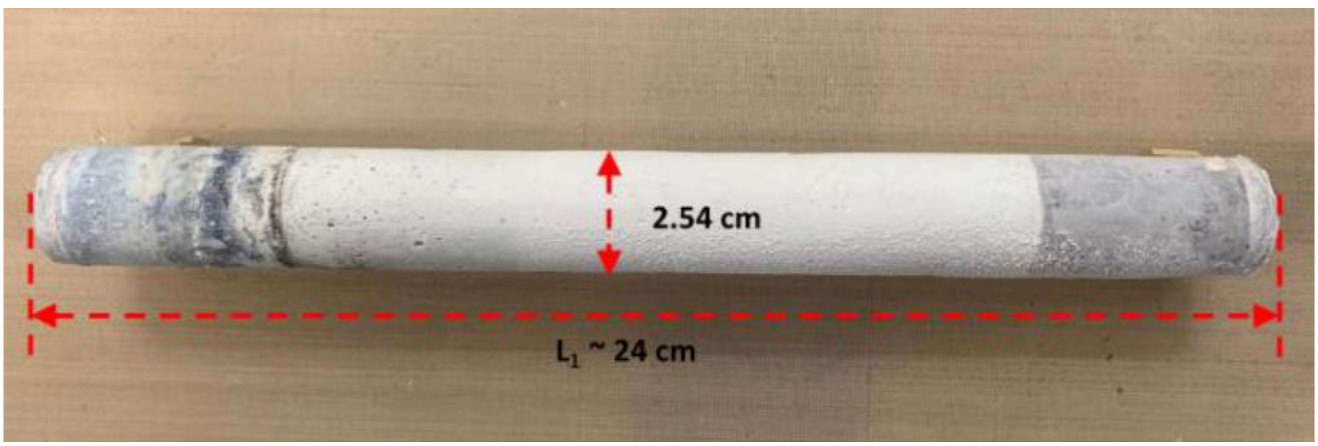

Figure 3: Post-heat-treated catalytic tube substrate.

To achieve high permeance of hydrogen, the hydrogen-selective layer on the substrate must be as thin as possible. The Bettergy team has been developing what is termed a zeolite nanosheet laminated membrane (ZNLM); they have succeeded in synthesizing a silicalite ZNLM on catalyst-alumina composite disc supports (Si-ZNLM-Cat) with minimized defects as indicated by favorable H_2/CO_2 separation selectivity of less than 0.5; also, the Si-ZNLM-Cat demonstrated enhanced CO conversion when operated as a membrane reactor for the WGS reaction at 500°C and 10 bar reaction pressure. The results indicate that ZNLM-Cat can be fabricated with reasonably well-preserved catalytic activity and membrane integrity for high-temperature WGS in a membrane reactor configuration. Figure 4 shows scanning electron microscopy (SEM) image of the Si-ZNLM on the catalytic disc support. Although the membrane surface appears to be covered by discrete zeolite particles, the Si-ZNLM is dense and continuous underneath, with uniform thickness of the membrane about 2.5 µm.

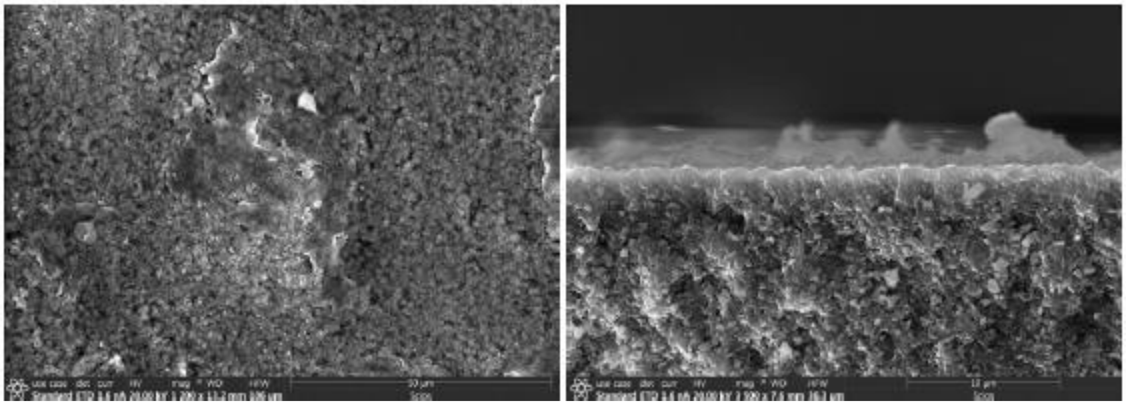

Figure 4: SEM images of the Si-ZNLM membrane: (left) surface and (right) cross-section.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	composite	composite
Materials of Fabrication for Support Layer	—	WGS catalyst	WGS catalyst
Nominal Thickness of Selective Layer	µm	10-20	10-20
Membrane Geometry	—	tubular	multichannel
Max Trans-Membrane Pressure	bar	10-30	30
Hours Tested without Significant Degradation	—	500	1,000
Manufacturing Cost for Membrane Material	$\$/m^2$	1,000	355-657
Membrane Performance			
Temperature	°C	350-550	400-500
H_2 Pressure Normalized Flux	GPU or equivalent	150	50-250
H_2/H_2O Selectivity	—	N/A	N/A
H_2/CO_2 Selectivity (Dense layer thickness)	—	>50	>75
H_2/H_2S Selectivity (Dense layer thickness)	—	N/A	N/A
Sulfur Tolerance	ppm	200	500
Type of Measurement	—	mixed	mixed
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	counter flow	
Packing Density	m^2/m^3	n/a	
Shell-Side Fluid	—	retentate	
Syngas Flowrate	kg/hr	0.21	
CO_2 Recovery, Purity, and Pressure	%/%/bar	80%, 80%, 20 bar	
H_2 Recovery, Purity, and Pressure	%/%/bar	80%, >95%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	1/1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	0.12	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, monolith, 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 atmosphere [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; 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 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 – Molecular sieving and activated diffusion.

Contaminant Resistance – TBD.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – TBD.

Waste Streams Generated – Hydrogen sulfide would remain in the retentate and must be separated. This may result in a waste stream containing H_2S.

Process Design Concept – See Figure 1.

Proposed Module Integration – TBD.

The composition of the gas entering the module:

Pressure	Temperature	Composition (Dry) vol%						
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435.1	842	15.95	49.75	0.12	1.15	32.55	0.46	0.02

technology advantages

- The novel pre-combustion CO_2 capture technology can be used in current gasification plants or future IGCC plants for industrial H_2 production while simultaneously capturing CO_2.
- Bettergy's CMR system offers substantial simplification of the CO_2 capture process, reduction in the cost of CO_2 capture, and increased energy efficiency, providing economic and environmental benefits for the general public.
- Microchannel reactors facilitate favorable operating temperature profiles in the reactor.
- Microchannel reactors minimize catalyst loading and limit pressure drop.
- Microchannel reactors provide optimized balance between capital cost and performance.

R&D challenges

- Optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate).
- Preparation of the H_2-selective composite zeolite thin layer membrane on the support/substrate.
- Development and optimization of WGS-CMR assemblies.
- "Trade-off" of membrane separation factor and catalyst activity, as governed by catalytic reaction intrinsic kinetics, gas diffusion mechanisms in the catalyst/membrane, and membrane properties.
- Fabrication of high-quality multi-channel catalytic substrates due to lack of satisfactory commercially available extruding machines.

status

Fabrication methods for single-channel and multi-channel tubular catalytic substrates have been developed, and successful formation of zeolite membrane layer on catalytic surfaces has been accomplished. Evaluation of performance has shown increased CO conversion via the WGS-CMR concept.

available reports/technical papers/presentations

"Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," Phase I final briefing/Phase II kickoff meeting, August 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12097&filename=Integrated+Multichannel+WGS+Catalytic+Membrane+Reactor+for+Pre-Combustion+Carbon+Capture.pdf*

"Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," Phase I kickoff meeting presentation, July 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12098&filename=Integrated+Multichannel+WGS+Catalytic+Membrane+Reactor+for+Pre-combustion+Carbon+Capture.pdf*

US Provisional Patent Application No. 63/150,253, "Integrated multichannel membrane reactor," 2021.