Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO$_2$ Capture (DE-FE0031632)

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Membrane Technology and Research, Inc.

DOE NETL Virtual Review Meeting
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Project Overview

Award name: Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO₂ Capture (DE-FE0031632)

Project period: 10/1/18 to 12/30/21
Funding: $2.0 million DOE; $0.5 million cost share ($2.5 million total)
DOE program manager: Carl Laird
Participants: MTR, Susteon, Energy & Environmental Research Center (EERC)

Project scope: Optimize Gen-2 Proteus membrane and develop modules capable of operation at 200°C; demonstrate membrane module performance processing coal-derived syngas during field test at EERC; optimize integration of membrane processes into IGCC with carbon capture

Project plan: The project is organized in three phases:

• **Budget Period 1/Year 1** – Gen-2 Proteus membrane optimized, high temperature module components identified
• **Budget Period 2/Year 2** – Gen-2 Proteus modules tested at MTR; fabricate field test skid
• **Budget Period 3/Year 3** – Install skid and conduct field test at EERC, analyze results, update TEA with field test performance and optimized membrane process design
Role of Participants

- **MTR** – project lead and liaison with DOE; responsible for membrane and module development; skid design, construction, installation and operation; will lead data analysis and all reporting to DOE

- **Susteon** (Raghubir Gupta, Cory Sanderson, Jim Zhou) – process optimization studies for integration of MTR’s membrane capture process in IGCC and TEA report

- **EERC** (Tyler Newman, Mike Swanson) – host site for field test in Budget Period 3 of project; with MTR, will coordinate system installation, operation, decommissioning, and data analysis
Membrane advantages:
- Can operate warm/hot to reduce the need for heat exchange
- CO₂ is maintained at pressure; less compression compared to standard AGR
- Water goes with fuel gas; reduces CO₂ dehydration costs
• Collaborated with Jim Black at DOE NETL and Peter Kabatek at WorleyParsons to analyze MTR process

• Compared to GE Gasifier with 2-stage Selexol (Case 2 of DOE Bituminous Baselines Study), MTR process shows 27 MWₜ net power improvement and 7.4% lower COE with Gen-1 Proteus membrane properties

• Both warm (H₂ membrane) and cold (CO₂ membrane) portions of process tested at NCCC
Background: H₂-Selective Proteus Membrane

• Temperature limit: 150°C
• Average H₂/CO₂ = 15
• NCCC field tests (2009 – 2016)
  – Stamps and lab-scale modules: 5,500 hours
  – Semi-commercial modules: 3,625 hours
• Additional industrial field tests
  – H₂ recovery in bio-waste to ethanol process
  – Syngas ratio adjustment in gas to liquids process

• Temperature limit: 200°C
• Average H₂/CO₂ = 30
• H₂/H₂S > 50
• H₂/CH₄, H₂/N₂, H₂/CO all >100
• Field test data consistent with lab results
Stages of Membrane Development

1) Membrane stamps (Budget Period 1)
   Area: 0.0030 m²
   Flow: 1 lb/h

2) Lab-scale module (Budget Period 2)
   Area: 0.130 m²
   Flow: 10 lb/h

3) Semi-commercial module (Budget Period 3)
   Area: 1 - 4 m²
   Flow: bench-scale (50 lb/h)

4) Commercial module
   Area: 20 – 50 m²
   Flow: field demonstration (500 lb/h)
Membrane and Module Component Screening

Module Component Exposure System

- Test conditions
  - Up to 1000 psig, 200°C
  - Inert gas, steam, or wet/dry gas mixtures (H₂, CO₂, N₂)

Recirculating Compressor System for Mixed-Gas Tests

- Booster compressor
- Feed bypass
- Feed stream
- Back pressure regulator
- Permeate (atm. or vacuum)
- Module
- 25 psia
- Relief valve 1,200 psig
- Permeate compressor
- Relief valve 30 psia
- Two-stage diaphragm compressor
- Vacuum pump to evacuate system
- Exhaust valve
- Make-up gas cylinder
Robust Gen-2 Proteus Membrane Developed with Target Performance

Temperature Cycling

Pressure Cycling with Nitrogen

Optimized Gen-2 Proteus Membrane has a $H_2/CO_2 = 37$
Gen-2 Proteus Production Scaled Up to Commercial Roll-to-Roll Equipment

MTR Commercial Casting Machine

Fabrication of Full-Length Module for Field Test

MTR R&D Coating Machine

Gen-2 Proteus Modules Developed in this Project
Bench-Scale Field Test at EERC

- Field test conditions confirmed early in BP2
  - Oxygen-blown fluidized bed gasifier
  - 300 - 500 psig
  - 30 – 35% H₂, 40 – 50% CO₂
  - Up to 3000 PPM H₂S

- Skid was fabricated in Northern California, arrived at EERC in January 2021

- Two MTR engineers were on-site from April 21 through May 1 for all field test activities

- Great support from EERC throughout project and field test
Gen-2 Proteus Field Test Performance

- Full parametric test matrix of temperature and feed syngas pressures was completed.
- Module was temperature cycled up to a simulated process upset condition 215°C at a syngas pressure of 300 psig.
- Initial/final 170°C $H_2$ permeance values in excellent agreement with MTR lab mixed gas value reported in Q10 report (255 gpu).
Post-Field Test Membrane Module Analysis

- Post-Field Test pure gas measurements in excellent agreement with pre-test values
- Dye test and autopsy results:
  - Membrane/spacer compatibility not an issue
    - No membrane pin-hole leaks
  - Module components can operate in syngas conditions
    - Spacers in excellent condition
    - Glue lines intact
- All post-field tests did not find evident of membrane or module degradation due to exposure to high temperature syngas conditions
• TEA report activities ramping up
  – Aspen Plus simulation of IGCC Case B5B set up and reviewed directly with NETL modeling team to ensure match of performance
    • Simulation also capable of producing $H_2$, $NH_3$, and/or syngas
  – TEA framework set up to calculate LCOE, matching B5B
    • TEA can also determine cost of $H_2$ from IGCC or ATR/SMR
  – MTR Dual Membrane Process will be evaluated with MDEA and WDP processes for desulfurization step
    • Processes chosen by Susteon after desulfurization review of 11 different technologies
  – Gen-2 Proteus membrane temperature and selectivity sensitivity studies
    • 150, 175, and 200°C updated membrane performance to find LCOE impact
Susteon and MTR have also evaluated several potential near term industrial applications for MTR membranes:

- **H₂ Purification and CO₂ capture from a Modular Hydrogen Generation System**
  - MTR Proteus and Orion (commercial CO₂-selective) membranes

- **CO₂ capture from Steam Methane Reformer Syngas**
  - Multiple process designs with Proteus and Polaris membranes

- **CO₂ capture from Autothermal Reformer Syngas**
  - Simulation of this process design will be included in TEA report

- **Removing blended H₂ from Natural Gas Pipelines**
  - Used DOE-NREL technical report NREL/TP-5600-51995 as a reference
  - Two MTR lower temperature H₂-selective membranes have potential for this application
Summary

• Membranes have some advantages for pre-combustion CO$_2$ capture and H$_2$ purification
• Gen-2 Proteus membrane has been made on roll-to-roll equipment with a H$_2$/CO$_2$ = 37
• Gen-2 Proteus membrane modules successfully test at EERC in syngas conditions up to 215°C
• Techno-Economic Analysis and other deliverable project reports are underway
Acknowledgements

• U.S. Department of Energy, National Energy Technology Laboratory
  – Carl Laird
  – Andy Aurelio
  – Bruce Lani

• Susteon
  – Raghubir Gupta
  – Cory Sanderson
  – James Zhou

• EERC
  – Tyler Newman
  – Mike Swanson
  – Joshua Stanislowski
• **MTR** will provide membrane, module, and membrane process expertise; make the membranes and modules required for this project; design and build a membrane skid for CO₂ capture from pre-combustion syngas; work with EERC to install and operate the skid at their site; and participate in process optimization studies and techno-economic analysis with Susteon. As the lead organization, MTR will also act as technical and administrative liaison with DOE.

• **Susteon** will conduct process optimization studies to understand the best integration of MTR’s membrane capture process into a syngas cleanup train including contaminants handling. Susteon will also work with MTR personnel to conduct the project techno-economic analysis.

• The **Energy and Environmental Research Center (EERC)** will be the host site for testing of MTR’s bench-scale system in the third year of the program. EERC will provide the test site, all utilities, and syngas delivery and disposal to the project. EERC engineers will also work with MTR to design, install and operate the bench skid.
## FE31632 Gantt Chart

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