



The National Carbon Capture Center  
at the Power Systems Development Facility

**Topical Report  
Budget Period Three**

**Reporting Period: August 1, 2016 – July 31, 2017  
Project Period: June 6, 2014 – May 31, 2019**

DOE Cooperative Agreement  
DE-FE0022596

Prepared by:  
Southern Company Services, Inc.  
Power Systems Development Facility  
P.O. Box 1069, Wilsonville, AL 35186  
Phone: 205-670-5840  
Fax: 205-670-5843  
<http://www.NationalCarbonCaptureCenter.com>

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Phone: 205-670-5840

Fax: 205-670-5843

E-mail: [nccc@southernco.com](mailto:nccc@southernco.com)

<http://www.NationalCarbonCaptureCenter.com>

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## **Abstract**

The National Carbon Capture Center (NCCC) at the Power Systems Development Facility supports the Department of Energy (DOE) goal of promoting the United States' energy security through reliable, clean, and affordable energy produced from coal. Work at the NCCC supports the development of new power technologies and the continued operation of conventional power plants under CO<sub>2</sub> emission constraints.

The NCCC includes multiple slipstream units that allow development of CO<sub>2</sub> capture concepts using coal-derived flue gas and syngas in industrial settings. Because of the ability to operate under a wide range of flow rates and process conditions, research at the NCCC can effectively evaluate technologies at various levels of maturity and accelerate their development to commercialization.

During the Budget Period Three reporting period, spanning from August 1, 2016, through July 31, 2017, efforts at the NCCC focused on post-combustion CO<sub>2</sub> capture, gasification, and pre-combustion CO<sub>2</sub> capture technology development. Testing was conducted at the NCCC's Post-Combustion Carbon Capture Center with membrane technologies, advanced solvents and solvent systems, enzymes, and aerosol mitigation equipment. The gasification process was also operated for evaluation of syngas utilization processes, catalysts, and sorbents. Pre-combustion CO<sub>2</sub> capture projects tested included membrane and sorbent technologies.

## **Acknowledgement**

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## Table of Contents

Disclaimer.....	iii
Abstract.....	iv
Acknowledgement .....	v
List of Figures .....	vii
List of Tables .....	viii
List of Abbreviations .....	ix
1.0 Executive Summary.....	1
1.1 Post-Combustion CO <sub>2</sub> Capture Accomplishments .....	2
1.2 Gasification Technology Accomplishments .....	5
1.3 Pre-Combustion CO <sub>2</sub> Capture Accomplishments.....	5
2.0 Post-Combustion CO <sub>2</sub> Capture.....	7
2.1 GE Global Research Aminosilicone Solvent and Desorber Unit.....	8
2.2 Air Liquide Cold Membrane .....	9
2.3 SSTU MEA Baseline .....	11
2.4 NETL Membranes.....	12
2.5 Amine Emissions Studies.....	13
2.6 CCSI <sup>2</sup> MEA Baseline in PSTU .....	15
2.7 Trimeric/UT-Austin NO <sub>2</sub> Scrubbing .....	17
2.8 Gas Technology Institute Membrane Contactor.....	18
2.9 Future Post-Combustion Test Plans.....	19
3.0 Gasification .....	20
3.1 Southern Research Institute Fischer-Tropsch Catalyst and Steam Reformer.....	21
3.2 Water-Gas Shift and COS Hydrolysis Catalysts.....	22
3.3 Ohio State University Syngas Chemical Looping.....	22
4.0 Pre-Combustion CO <sub>2</sub> Capture .....	25
4.1 SRI International Polybenzimidazole Hydrogen Membranes .....	25
4.2 Membrane Technology & Research Proteus Membranes.....	27
4.3 Media & Process Technology Palladium-Based Hydrogen Membranes.....	29
4.4 TDA Research 0.1-MW CO <sub>2</sub> Sorbent System.....	32
5.0 Conclusions and Lessons Learned.....	35
5.1 Post-Combustion.....	35
5.2 Gasification .....	38
5.3 Pre-Combustion .....	39

## List of Figures

Figure 1. NCCC Facilities.....	2
Figure 2. Schematic of PC4 Test Facilities.....	7
Figure 3. GE Global Desorber Unit Installed in PSTU Structure.....	8
Figure 4. Air Liquide Cold Membrane Process Skids.....	10
Figure 5. Normalized CO <sub>2</sub> Permeance and CO <sub>2</sub> /N <sub>2</sub> Selectivity of Air Liquide Membrane Bundles.....	10
Figure 6. Schematic of SSTU.....	11
Figure 7. NETL Hollow Fiber Membrane Test Equipment.....	12
Figure 8. Screenshots of PDI Data before and after Baghouse Operation.....	13
Figure 9. Screenshot of ELPI+ Results during Typical SSTU Operation.....	14
Figure 10. MEA Concentration in Treated Flue Gas Stream before and after Baghouse Installation as Sampled by the FTIR.....	14
Figure 11. Initial Reduction in CO <sub>2</sub> Capture Rate Confidence Interval Width Resulting from CCSI <sup>2</sup> MEA Baseline Testing.....	16
Figure 12. Secondary Reduction in CO <sub>2</sub> Capture Rate Confidence Interval Width Resulting from CCSI <sup>2</sup> MEA Baseline Testing.....	17
Figure 13. NO <sub>2</sub> Removal and Sulfite Concentration in Pre-Scrubber during Trimeric/UT-Austin Testing.....	18
Figure 14. Gas Technology Institute Membrane Contactor Skids Installed at the PC4.....	19
Figure 15. Schematic of NCCC Gasification Process.....	20
Figure 16. Southern Research Fischer-Tropsch Catalyst and Steam Reformer Equipment.....	21
Figure 17. Typical SCL Reducer Outlet Gas Composition During Syngas Operation.....	23
Figure 18. Syngas Conversion in the SCL Reducer.....	24
Figure 19. Hydrogen Concentration in SCL Oxidizer Outlet Gas.....	24
Figure 20. Schematic of Pre-Combustion CO <sub>2</sub> Capture Facilities.....	25
Figure 21. SRI International PBI Membrane Skid.....	26
Figure 22. Comparison of Hydrogen/CO <sub>2</sub> Selectivity for GEN-1 and GEN-2 PBI Modules.....	26
Figure 23. Hydrogen Recovery of PBI Membrane with Varying Stage Cuts.....	27
Figure 24. Syngas Feed Composition for MTR's Four-Inch Membrane Module.....	28
Figure 25. Permeate Stream Composition for MTR's Four-Inch Membrane Module.....	28
Figure 26. MPT Membrane Bundles and Housing Units.....	29
Figure 27. Hydrogen Concentration of Feed and Permeate Streams of MPT's Membrane Bundle A.....	30
Figure 28. Hydrogen Concentration of Feed and Permeate Streams of MPT's Membrane Bundle B.....	31
Figure 29. TDA Research CO <sub>2</sub> Sorbent Test Skids.....	32
Figure 30. Carbon and CO <sub>2</sub> Capture Results for TDA Sorbent Technology.....	33
Figure 31. Working Capacity of the TDA Sorbent over Time.....	34

### List of Tables

Table 1. Post-Combustion CO <sub>2</sub> Capture Technologies Tested in Budget Period Three .....	3
Table 2. Gasification Technologies Tested in Budget Period Three.....	5
Table 3. Pre-Combustion CO <sub>2</sub> Capture Technologies Tested in Budget Period Three.....	6
Table 4. Average Values of PC4 Flue Gas Components and Conditions .....	7
Table 5. Average Syngas Composition and Carbon Conversion for G-5 Steady State Periods .....	20
Table 6. Hydrogen Permeance of MPT's Palladium Membranes during Lab Regeneration.....	31
Table 7. Operating Parameters for TDA Sorbent Process.....	33
Table 8. Comparison of Design and Actual Conditions for TDA Testing .....	34

## List of Abbreviations

BP3	Budget Period Three
CCSI	Carbon Capture Simulation Initiative
CCSI <sup>2</sup>	Carbon Capture Simulation for Industry Impact
CO	Carbon Monoxide
COS	Carbonyl Sulfide
CSTR	Continuous Stirred Tank Reactor
DOE	Department of Energy
ELPI+	Electric Low Pressure Impactor
F-T	Fischer-Tropsch
FTIR	Fourier Transform Infrared Spectrometer
G-5	Gasification Run 5
GC	Gas Chromatograph
GPU	Gas Permeation Unit
GTI	Gas Technology Institute
H <sub>2</sub> S	Hydrogen Sulfide
IGCC	Integrated Gasification Combined Cycle
MEA	Monoethanol Amine
MPT	Media & Process Technology
MTR	Membrane Technology & Research
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
NO	Nitrogen Oxide
NO <sub>2</sub>	Nitrogen Dioxide
OSU	Ohio State University
PBI	Polybenzimidazole
PC4	Post-Combustion Carbon Capture Center
PDI	Phase Doppler Interferometer
PO-1 through 6	Post-Combustion Runs 1 through 6
PSDF	Power Systems Development Facility
PSTU	Pilot Solvent Test Unit
SCL	Syngas Chemical Looping
SCU	Syngas Conditioning Unit
SR	Southern Research
SRI	SRI International
SSTU	Slipstream Solvent Test Unit
UT-Austin	University of Texas at Austin
WGS	Water-Gas Shift

## **1.0 EXECUTIVE SUMMARY**

The National Carbon Capture Center (NCCC) at the Power Systems Development Facility is a key component of the Department of Energy's (DOE's) strategy in promoting the United States' economic, environmental, and energy security through reliable, clean, and affordable power produced from coal. Located in Wilsonville, Alabama, the NCCC is a cost-effective, flexible test center for evaluating the critical components of advanced CO<sub>2</sub> capture and power generation processes from third-party technology developers, including government entities, industry, and universities. Work at the NCCC supports the development of new power technologies and the continued operation of conventional power plants under CO<sub>2</sub> emission constraints.

### ***Project Partnership with DOE***

The DOE Office of Fossil Energy's National Energy Technology Laboratory (NETL), in cooperation with Southern Company, established the NCCC in 2009 to become a cornerstone for U.S. leadership in advanced clean coal technology development. After the successful completion of the first contract period, which comprised testing and advancement of numerous CO<sub>2</sub> capture and gasification support technologies, the DOE renewed its support of the project with another cooperative agreement spanning from June 2014 through May 2019. As of July 2017, due to changes in the Office of Fossil Energy priorities, the DOE will no longer support development of gasification and pre-combustion CO<sub>2</sub> capture technologies, although work to progress post-combustion CO<sub>2</sub> capture technologies is expected to continue through the end of the current cooperative agreement.

### ***Reporting Period***

This report covers the work performed during Budget Period Three (BP3), from August 1, 2016, through July 31, 2017, of the NCCC's second cooperative agreement with DOE, DE-FE0022596.

### ***Project Mission and Approach***

Offering a world-class neutral test facility and a highly specialized staff, the NCCC accelerates the commercialization of advanced technologies to enable fossil fuel-based power plants to achieve near-zero emissions. In undertaking its mission, the NCCC has been involved in a range of activities in the areas of post-combustion CO<sub>2</sub> capture, gasification, and pre-combustion CO<sub>2</sub> capture to develop the most promising technologies for future commercial deployment.

The NCCC houses two test sites, shown in Figure 1. To develop CO<sub>2</sub> capture technologies for existing fossil-fueled power plants, the NCCC operates the Post-Combustion Carbon Capture Center (PC4), which utilizes flue gas from a commercially dispatched supercritical coal-fired power plant. The PC4 includes bench-scale and pilot-scale solvent test units and test bays for technology developer skids. At the original Power Systems Development Facility site, the NCCC has operated its pilot Transport Gasifier plant to produce syngas for slipstream testing of gasification and pre-combustion CO<sub>2</sub> capture technologies at bench- and pilot-scales.



Figure 1. NCCC Facilities

## 1.1 Post-Combustion CO<sub>2</sub> Capture Accomplishments

During the reporting period, the PC4 operated in two test runs, supporting multiple technology developer projects, which are listed in Table 1. Operation was conducted with bench- and pilot-scale test skids and with the NCCC's Slipstream Solvent Test Unit (SSTU) and Pilot Solvent Test Unit (PSTU). To investigate the issue of solvent emissions, aerosol sampling was conducted with specialized measurement devices, the Electric Low Pressure Impactor (ELPI+) a Phase Doppler Interferometer (PDI), and a Fourier Transform Infrared (FTIR) analyzer. The post-combustion runs conducted in BP3 included:

- PO-5, beginning in Budget Period 2, from May 18, 2016, through February 27, 2017
- PO-6, occurring from June 12, 2017, and continuing into Budget Period 4 (through mid-August 2017)

**Table 1. Post-Combustion CO<sub>2</sub> Capture Technologies Tested in Budget Period Three**

<i>Venue</i>	<i>Technology Tested</i>	<i>Hours</i>
<i>Run PO-5</i>		
Pilot-Scale	GE Global Solvent and Desorber w/PSTU	915
	Air Liquide Cold Membrane	2,204
Bench-Scale	SSTU Operation with Monoethanol Amine (MEA)	980
	NETL Membranes	1,311
	Amine Emissions Studies	205
<i>Run PO-6</i>		
Pilot-Scale	PSTU Operation with MEA for NETL’s Carbon Capture Simulation for Industry Impact (CCSI <sup>2</sup> )	620
	Trimeric Corporation/University of Texas at Austin (UT-Austin) Nitrogen Dioxide (NO <sub>2</sub> ) Scrubbing	1,147
	Gas Technology Institute (GTI) Hollow Fiber Membrane Contactor	In progress
Bench-Scale	SSTU Operation with MEA	In progress

Accomplishments in the post-combustion CO<sub>2</sub> capture program are highlighted below.

***GE Global Research Aminosilicone Solvent and Desorber***

GE Global tested its GAP-1 solvent in the PSTU for over 900 hours of operation using two desorption designs: GE’s Continuous Stirred Tank Reactor (CSTR), and the PSTU regenerator column. Both desorption options achieved 95% CO<sub>2</sub> capture efficiency, although for operation with the CSTR a solvent-to-CO<sub>2</sub> ratio of 4 was required, while for operation with the regenerator, a 0.5 solvent-to-CO<sub>2</sub> ratio was needed. The PSTU regenerator column was found to be more robust in regard to solvent entrainment, and with this configuration, the GAP-1 solvent exhibited a 25% increased working capacity, and 10% reduction in specific steam duty as compared to MEA, at 5.5°C (10°F) lower desorption temperature. The first year CO<sub>2</sub> removal cost for the aminosilicone-based carbon-capture process was estimated at \$48/ton CO<sub>2</sub> using a steam stripper column, which represented a 20% reduction compared to MEA.

***Air Liquide Cold Membrane***

Air Liquide continued testing of its cold membrane process and evaluation of membrane materials, building on previous operation in 2015. In the PO-5 run, Air Liquide additionally tested a prototype membrane of next generation polyimide material, PI-2. The PI-2 membrane achieved eight to nine times the CO<sub>2</sub> permeance of the commercial bundle, and demonstrated stable CO<sub>2</sub> recovery and purity over more than 700 hours of operation, which included multiple

shutdowns. Further testing is planned to begin in late 2017 at the PC4 under a new DOE contract, with the focus on scale-up with the PI-2 material and commercial bundle testing.

### ***Slipstream Solvent Test Unit***

Based on the previous commissioning of the SSTU, several modifications were made to improve operating performance. Further operation with MEA during run PO-5 demonstrated more stable operations, and testing in run PO-6 was underway to identify optimal conditions.

### ***NETL Membranes***

As a continuation of previous testing in 2015, NETL operated its post-combustion membrane skid to identify materials with acceptable CO<sub>2</sub> separation performance in the presence of water vapor and minor contaminants. Due to software issues and equipment deficiencies, however, the testing did not produce useful data. NETL plans for additional testing in 2018.

### ***Amine Emissions Studies***

Solvent emissions measurements were taken during operation of the SSTU with MEA solvent to further quantify the effects of an upstream baghouse on flue gas aerosols and subsequently on emissions. In addition to the ELPI+ measurements for aerosol size and count, a PDI and an FTIR were used on the SSTU treated flue gas stream. The data demonstrated a significant drop in solvent emissions with the baghouse in operation.

### ***CCSI<sup>2</sup>MEA Baseline Testing in the PSTU***

The PSTU was operated with MEA baseline solvent in support of the Carbon Capture Simulation for Industry Impact, which is the second phase of the Carbon Capture Simulation Initiative (CCSI). The test campaign built on previous testing, using a Bayesian experimental design to reduce uncertainty in the carbon capture model. The effectiveness of the experimental design methodology was clearly demonstrated for steady-state operations, and the CCSI<sup>2</sup> group is continuing work on utilizing dynamic data taken during the run.

### ***Trimeric/UT-Austin NO<sub>2</sub> Scrubbing***

Trimeric and UT-Austin completed testing of a chemical process for removal of NO<sub>2</sub> from amine-based solvent systems in order to minimize solvent losses. The process involves the use of the low-cost chemical thiosulfate in an SO<sub>2</sub> pre-scrubber. Testing showed that the NO<sub>2</sub> removal rate strongly correlated with the sulfite concentration, which was controlled by the amount of thiosulfate added. Greater than 95% removal of NO<sub>2</sub> was achieved.

### ***Gas Technology Institute Hollow Fiber Membrane Contactor***

GTI completed installation and began testing of a hollow fiber gas-liquid membrane contactor, which is a hybrid system combining the advantages of membrane gas separation and solvent absorption mechanisms. Initial testing demonstrated 90% CO<sub>2</sub> capture and CO<sub>2</sub> product purity greater than 97%. Testing was planned to continue through mid-August 2017.

## 1.2 Gasification Technology Accomplishments

To provide syngas for developer technology testing, gasification run G-5 was conducted from March 24 through April 30, 2017, with 900 hours of operation achieved. The run utilized Powder River Basin subbituminous coal and allowed for over 1,800 hours of testing by third-party gasification technology developers. Table 2 summarizes the testing completed by gasification technology developers, and highlights of the testing are discussed below.

**Table 2. Gasification Technologies Tested in Budget Period Three**

<i>Technology Tested</i>	<i>Hours</i>
Southern Research Fischer-Tropsch Catalyst	125
Southern Research Steam Reformer	125
Water-Gas Shift Catalyst	774
Carbonyl Sulfide Hydrolysis Catalyst	776
Ohio State University Syngas Chemical Looping	33

### ***Southern Research (SR) Fischer-Tropsch (F-T) Catalyst and Steam Reformer***

Southern Research incorporated a four-fold scale-up of the previously tested F-T catalyst and tested a high-temperature steam reformer for the first time. Both technologies achieved performance targets. The F-T catalyst showed jet fuel-range hydrocarbon selectivity of 75% with almost no undesired long-chain hydrocarbons (above C22). The reformer demonstrated up to 90% conversion of methane and nearly complete conversion of tars in the presence of hydrogen sulfide (H<sub>2</sub>S).

### ***Water-Gas Shift (WGS) and Carbonyl Sulfide (COS) Hydrolysis Catalysts***

Operation of WGS and COS hydrolysis catalysts continued for demonstration of long-term durability. Following the G-5 gasification run, the WGS catalyst had accumulated 6,900 hours of operation, and the COS hydrolysis catalyst had accumulated 4,000 hours.

### ***Ohio State University (OSU) Syngas Chemical Looping (SCL)***

OSU tested the high-pressure SCL process with syngas feed while circulating oxygen carrier particles, demonstrating 70% syngas conversion. The SCL process operated with steam for a short period and produced hydrogen for the first time.

## 1.3 Pre-Combustion CO<sub>2</sub> Capture Accomplishments

Pre-combustion CO<sub>2</sub> capture operation during the G-5 gasification run comprised over 1,700 hours of technology developer testing, as summarized in Table 3 and described below.

**Table 3. Pre-Combustion CO<sub>2</sub> Capture Technologies Tested in Budget Period Three**

<i>Technology Tested</i>	<i>Hours</i>
SRI International Polybenzimidazole Hydrogen Membranes	573
Membrane Technology & Research Proteus™ Hydrogen Membranes	275
Media & Process Technology Palladium-Based Hydrogen Membranes	156
TDA Research CO <sub>2</sub> Sorbent	740

***SRI International (SRI) Polybenzimidazole (PBI) Hydrogen Membranes***

SRI conducted the first syngas testing of a hydrogen membrane fabricated with spun hollow fibers of the temperature- and chemical-resistant polymer PBI. Testing confirmed that greater than 90% recovery of CO<sub>2</sub> is possible at operating temperatures above 375°F (190°C).

***Membrane Technology & Research (MTR) Proteus Hydrogen Membranes***

MTR continued evaluation of Proteus hydrogen membranes, conducting long-term testing with a four-inch module. The membrane module enriched the hydrogen concentration in the permeate to roughly five times the feed concentration. The membrane module performance showed no deterioration over the last two gasification runs, indicating high quality of the module.

***Media & Process Technology (MPT) Palladium-Based Hydrogen Membranes***

MPT conducted the first test of a stand-alone, multi-tube palladium membrane for hydrogen separation. In MPT’s previous palladium membrane testing, a single tube was used as a polishing step of the permeate of the carbon molecular sieve. During G-5 hydrogen permeance values were lower than expected due to the effects of tar. However, MPT demonstrated that the permeance could be restored in the lab with air treatment at raised temperatures.

***TDA Research CO<sub>2</sub> Sorbent***

After completing several successful campaigns at the NCCC with CO<sub>2</sub> sorbent technology, TDA scaled up testing of the CO<sub>2</sub> sorbent process to a small pilot-scale unit tested in G-5. By optimizing the process cycle to allow faster cycling, TDA reduced the bed size by half in the 0.1-MW skid. The unit consistently achieved at least 90% carbon capture.

## 2.0 POST-COMBUSTION CO<sub>2</sub> CAPTURE

The PC4 utilizes flue gas from Plant Gaston Unit 5, a base-loaded, 880-MW supercritical pulverized coal boiler. The unit meets all environmental requirements utilizing state-of-the-art controls; thus, the flue gas extracted for testing is fully representative of commercial conditions. As shown in Figure 2, the PC4 provides sites for technology developers' bench-scale and pilot-scale test units. The Pilot Solvent Test Unit and the Slipstream Solvent Test Unit are fully integrated systems for comprehensive solvent characterization at pilot- and bench-scale, respectively. An air dilution system is also available for CO<sub>2</sub> capture testing under simulated natural gas flue gas conditions.

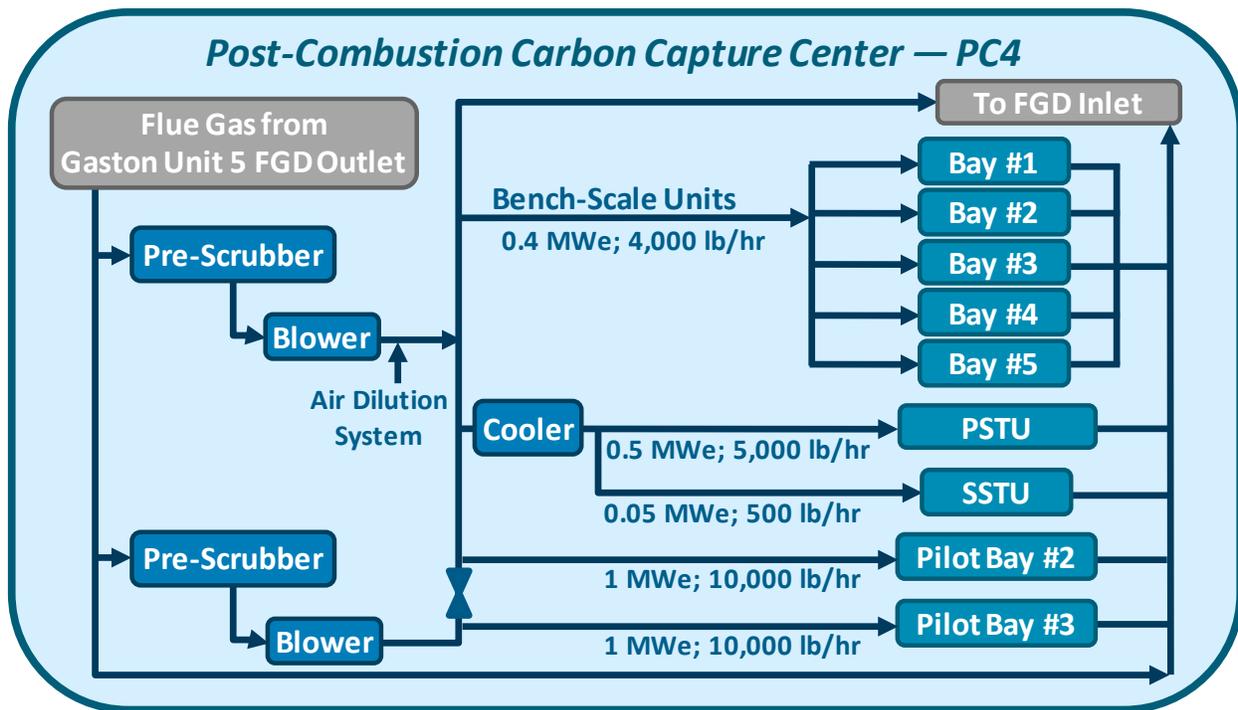


Figure 2. Schematic of PC4 Test Facilities

Table 4 lists the average composition and conditions of the flue gas used for testing at the PC4.

Table 4. Average Values of PC4 Flue Gas Components and Conditions

Flue Gas Component	Value
CO <sub>2</sub> , vol%	12.1
Oxygen, vol%	7.1
H <sub>2</sub> O, vol%	7.6
Nitrogen Oxide (NO), ppm	41.0
NO <sub>2</sub> , ppm	6.5
Temperature, °F	155
Pressure, inH <sub>2</sub> O	20

## 2.1 GE Global Research Aminosilicone Solvent and Desorber Unit

GE Global completed work to demonstrate a CO<sub>2</sub> capture process using its GAP-1 aminosilicone solvent. Compared to alkanolamines such as MEA, aminosilicones possess properties that substantially decrease the cost of solvent-based CO<sub>2</sub> capture, including lower vapor pressures, higher boiling points, greater thermal stability, and lower heat capacity. In addition, the replacement of water with a nonvolatile co-solvent, triethleneglycol, results in a substantial energy savings. In conjunction with the solvent development, GE developed a continuous stirred tank reactor for CO<sub>2</sub> desorption as an alternative to traditional column strippers. Compared to a stripper column, the CSTR is smaller and lower in cost. Based on promising lab results, GE scaled up its technology for testing with the PSTU. Figure 3 shows the GE desorber as installed in the PSTU structure.



**Figure 3. GE Global Desorber Unit Installed in PSTU Structure**

Through lab testing, GE found that though its solvent exhibited high thermal stability at elevated temperatures, the stability dropped as CO<sub>2</sub> loading increased due to urea formation. Adding water limited the urea formation reaction and hence reduced degradation. Therefore, for initial testing at the PC4, the water content of the solvent solution was targeted at 5 to 10%. Furthermore, water was found to be an effective way to enable steam stripping, lower desorption temperature, and hence further reduce thermal degradation. Steam stripping also increased the solvent working capacity by 30% due to more efficient desorption. In light of these advantages to steam stripping, GE expanded the test scope from testing the GAP-1 solvent and CSTR to also testing the solvent with the PSTU regenerator, a standard stripper column.

Solvent testing in the integrated PSTU/CSTR system was conducted during the PO-5 run. Several issues were encountered during early operation, including the tendency of solvent foaming in the CSTR, which resulted in solvent carryover and loss. Through experimentation, it

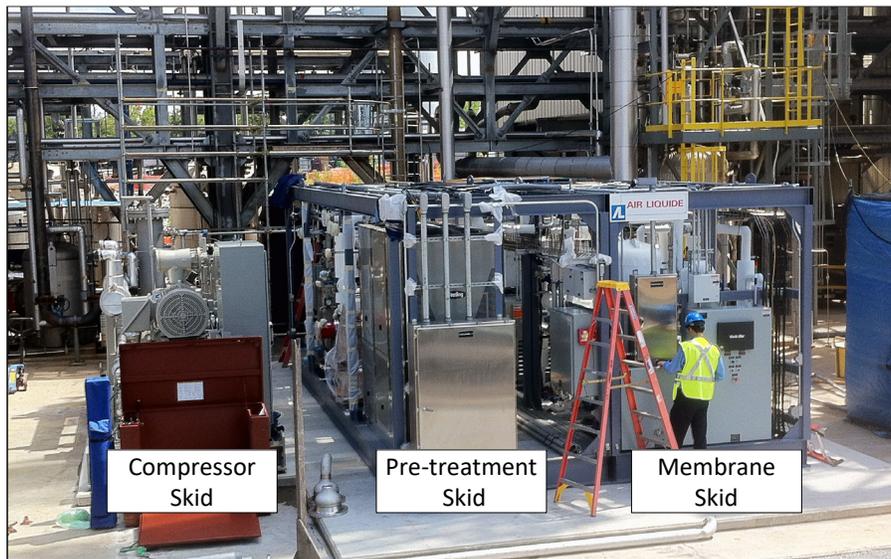
was determined that foaming and solvent carryover were minimized by maintaining the water concentration at 5% or less while operating the CSTR at 7 psig. The PSTU/CSTR operation consisted of more than 500 hours of operation with desorption temperatures of 110 to 130°C (230 to 265°F), solvent-to-CO<sub>2</sub> molar ratios of 1.5 to 4, and flue gas flow rates ranging from 2,000 to 5,000 lb/hr. The system demonstrated 95% CO<sub>2</sub> capture efficiency at a solvent-to-CO<sub>2</sub> molar ratio of 4 and desorption temperature of 110°C (230°F), and yielded 65% CO<sub>2</sub> capture efficiency at a solvent-to-CO<sub>2</sub> molar ratio of 0.5 and desorption temperature of 120°C (248°F).

After the PSTU/CSTR operation objectives were achieved, the system was switched to PSTU-only operation with the standard regenerator, a steam stripping column. Fresh solvent was used so that performances could be compared directly to that of PSTU/CSTR operation. The PSTU regeneration column was found to be more robust in regard to solvent entrainment, allowing water contents up to 35%. Under stoichiometric conditions, CO<sub>2</sub> capture efficiency was between 90 and 95% at a solvent-to-CO<sub>2</sub> molar ratio of 0.5, a desorption temperature of 235°F, a pressure of 2 psig, and a water content of 19 wt%. Both CO<sub>2</sub> capture efficiency and specific duty reached optimum conditions at 18 wt% H<sub>2</sub>O. Little amine degradation (less than 0.5 wt%/day) was recorded over 350 hours of operation. Controlled water addition to the solvent decreased the desorption temperature, thermal degradation, and improved the CO<sub>2</sub> working capacity due to more efficient absorption and desorption processes. Under these conditions, the GAP-1 solvent exhibited a 25% increased working capacity, and 10% reduction in specific steam duty as compared to MEA, at 5.5°C (10°F) lower desorption temperature.

GE updated its capture system process models using the data from PSTU testing, and performed a techno-economic analysis for a 550-MW coal fired power plant. The first year CO<sub>2</sub> removal cost for the aminosilicone-based carbon-capture process was estimated at \$48/ton CO<sub>2</sub> using a steam stripper column. This represented a 20% reduction compared to MEA, primarily due to lower overall capital cost. The estimated cost of CO<sub>2</sub> capture using the CSTR was dominated by the economics of the solvent make-up required by a higher degradation rate. The steam stripper column would be preferred due to higher desorption efficiency and lower solvent make-up rates. Further cost reductions would be expected from reductions in the solvent manufacturing cost, process optimization, and improvements in solvent stability and CO<sub>2</sub> working capacity with a next generation aminosilicone solvent.

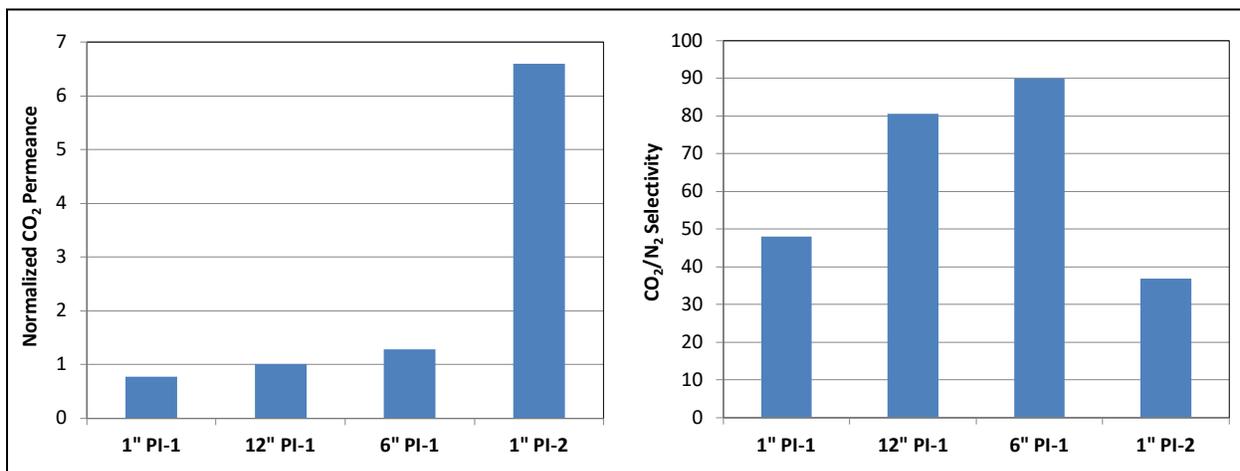
## 2.2 Air Liquide Cold Membrane

Air Liquide is developing a CO<sub>2</sub> capture process using hollow fiber membranes operating at sub-ambient temperatures. Air Liquide's lab testing showed that these membranes, when operated at temperatures below -20°C (-4°F), yield two to four times increase in CO<sub>2</sub>/nitrogen selectivity with minimal CO<sub>2</sub> permeance loss compared to ambient temperature values. Performance data were used to design a 0.3-MW small pilot-scale process, shown in Figure 4, to demonstrate commercial size membrane performances using actual flue gas. Two materials are being evaluated, a commercially available membrane from AL, PI-1 material, and a next generation polyimide membrane material (PI-2) for application in the cold membrane hybrid process.



**Figure 4. Air Liquide Cold Membrane Process Skids**

Following initial operation in 2015, Air Liquide operated the process during the PO-5 run with parametric tests on both 6-inch and 12-inch PI-1 membrane bundles and a 1-inch PI-2 membrane bundle. Figure 5 presents the test results for the three types of bundles. As demonstrated by the CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity values of the PI-1 bundles, the 6-inch configuration is the most ideal of the three. As expected, the 1-inch PI-2 bundle showed superior CO<sub>2</sub> permeance (more than 6.5 times higher) than the PI-1 bundles. However, the CO<sub>2</sub>/N<sub>2</sub> selectivity for the PI-2 bundle was lower than all of the PI-1 bundles. The data suggested further improvement could be realized with scale up of the PI-2 bundle to 6 or 12 inches.



**Figure 5. Normalized CO<sub>2</sub> Permeance and CO<sub>2</sub>/N<sub>2</sub> Selectivity of Air Liquide Membrane Bundles**

Other findings from these parametric tests include the following:

- Membrane bundle performance improved as the temperature decreased from -45°C (-49°F) down to -50°C (-58°F).

- Arrangement with two bundles in series did not show better performance than single bundles.
- Testing under various flue gas feed pressures, permeate pressures, and sweep gas flow rates showed that the 6-inch bundle was superior and exhibited the most ideal counter-current flow behavior.
- Analysis of flue gas contaminants showed that impurities such as mercury, selenium, and NO<sub>x</sub> were reduced to levels below detection limits in the membrane feed, due to their combined removal in the pretreatment condensates, dryer bed, and activated alumina bed.

Under a new DOE contract, Air Liquide plans for additional testing focused on scale-up with the PI-2 material to 6-inch bundles and long-term testing targeted for 500 hours at 90% capture. Air Liquide is also planning for large-scale testing at 25 to 30 MWe in the future.

### 2.3 SSTU MEA Baseline

The NCCC's SSTU provides for testing of solvents that are in early stages of development and solvents that are only available in amounts smaller than the 4,000 gallons required for the PSTU. The unit, shown in Figure 6, was commissioned in late 2015 with MEA, and following system modifications, additional tests were conducted during the PO-5 run. MEA baseline testing is critical for future comparisons of solvent based technologies that may be tested with the SSTU.

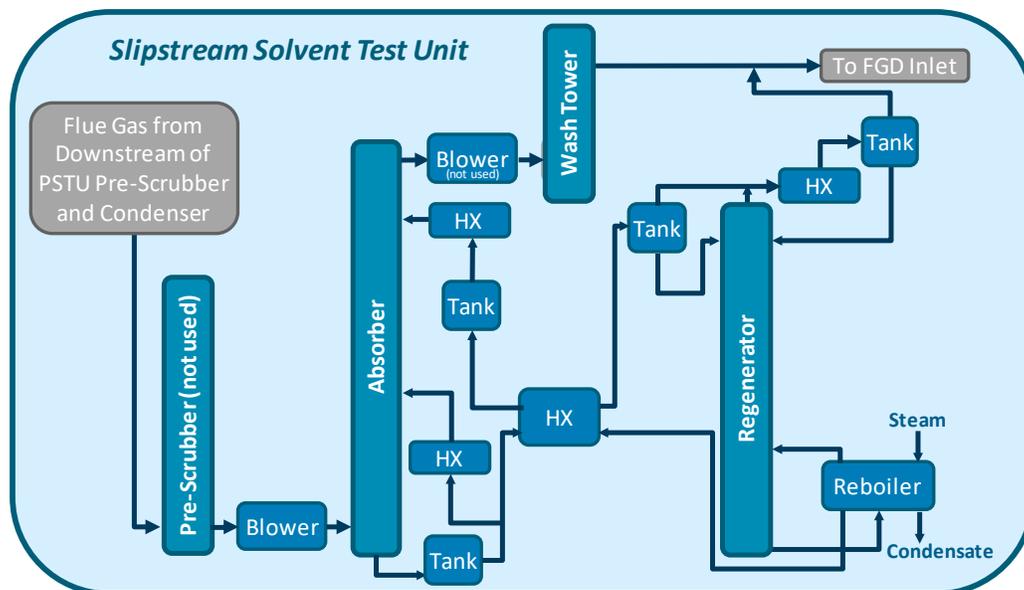


Figure 6. Schematic of SSTU

Lessons learned from operation in BP3 were:

- The CO<sub>2</sub> recovery rate improved dramatically with the addition of a blower upstream of the absorber, as opposed to the original as-delivered unit design containing a downstream blower.

- A positive pressure profile and its steady control are paramount for stable carbon capture in amine-based systems, and improvements to the backpressure control system were required for the completion of steady-state testing.
- A focus on instrumentation types, their installation, and the ability to evaluate their function with cross-checks incorporated into the system design are critical for ensuring data accuracy. The review of the as-provided pitot-style flow meters revealed improper installation that yielded erratic measurements and required redesign and replacement with V-cone style flow elements.

Additional testing with MEA was underway at the end of BP3 to further refine SSTU performance and identify the optimal conditions for maximum efficiency.

## 2.4 NETL Membranes

As a continuation of previous membrane testing, NETL operated its Post-Combustion Membrane Skid in 2016 during the PO-5 run. The skid, shown in Figure 7, allows testing of either hollow fiber modules or flat sheet modules and features automatic operation and flue gas pre-treatments of pressurizing, filtering, and dehumidifying. Mixed gas analysis is provided by a gas chromatograph. The PO-5 testing demonstrated the skid's capability of generating reliable data.



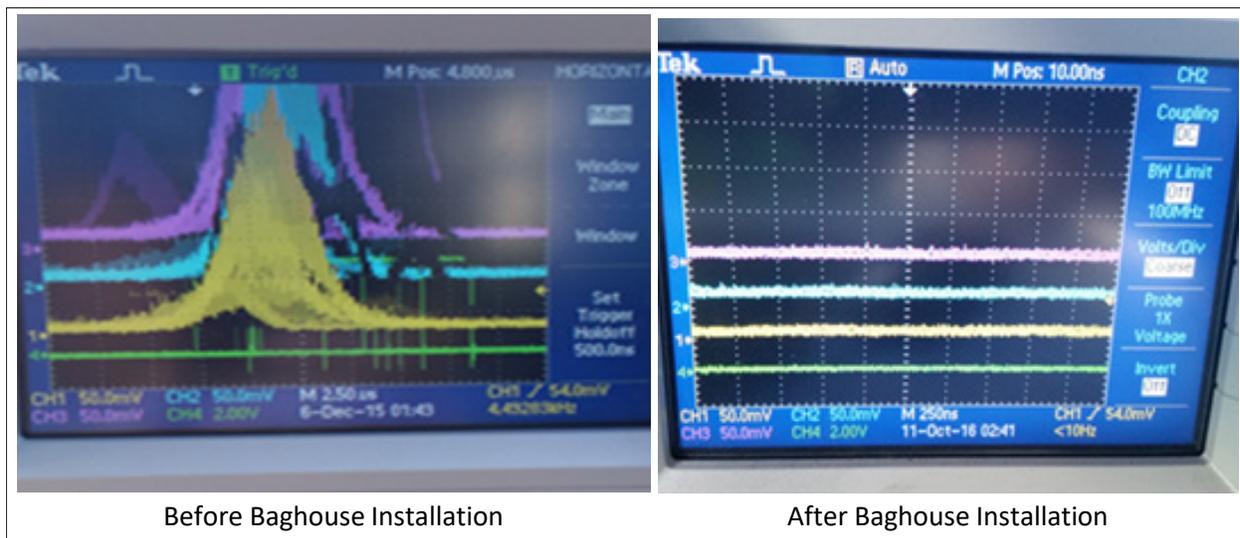
**Figure 7. NETL Hollow Fiber Membrane Test Equipment**

Testing in BP3 involved six membranes for a total of more than 1,300 hours. Some data was lost due to software and other issues. Because the gas chromatograph had required extensive maintenance throughout testing, and because it performed reliably for only short periods, NETL began efforts to procure a new Siemens Maxum II gas chromatograph (GC), as recommended by NCCC. NETL temporarily used a GC borrowed from the NCCC gasification process, but found that it did not provide the full suite of data required. Testing will resume during BP4 with refined membrane designs.

## 2.5 Amine Emissions Studies

Amine emissions from carbon capture systems in the form of aerosols leaving the absorber are a common problem with commercial solvent processes where  $\text{SO}_3$  is present in the flue gas. The formation of aerosols has been found to correlate with the concentration of  $\text{SO}_3$  present in the flue gas. Therefore, the NCCC has supported a series of tests to quantify the size and number of aerosols and to determine the effects of process equipment and conditions. Aerosol measurements were taken as baseline data in 2015 to compare against results obtained in 2016, when a new activated carbon injection baghouse was brought on-line at Gaston Unit 5, upstream of the PC4. The baghouse was installed to reduce heavy metals emissions, but has demonstrated the additional effect of removing most of the  $\text{SO}_3$  present.

During the MEA baseline test with the SSTU in late 2016, two separate teams used equipment to measure the aerosols present in the treated flue gas stream, which contribute to amine losses from the plant. Southern Research utilized the ELPI+ and a representative from UT-Austin operated the PDI. Initial data from the run confirmed a significant drop in aerosol count after the baghouse began operating. The ELPI+ data showed a shift in particle size distribution and particle count, but the PDI was unable to provide any indication of aerosols present because the particle sizes were below the detectable range of the instrument. Figure 8 provides two screenshots from the PDI from before and after the baghouse installation.



**Figure 8. Screenshots of PDI Data before and after Baghouse Operation**

Data from the ELPI+, presented in Figure 9, showed that the majority of particles were below 0.1 microns in diameter, which is below the detection limit of the PDI. The x-axis of the figure shows particle diameters in microns, and the y-axis shows the particle count. In addition to the drastic shift to smaller particle sizes observed, the total particle count dropped by three to five orders of magnitude compared to previous operation without the upstream baghouse.

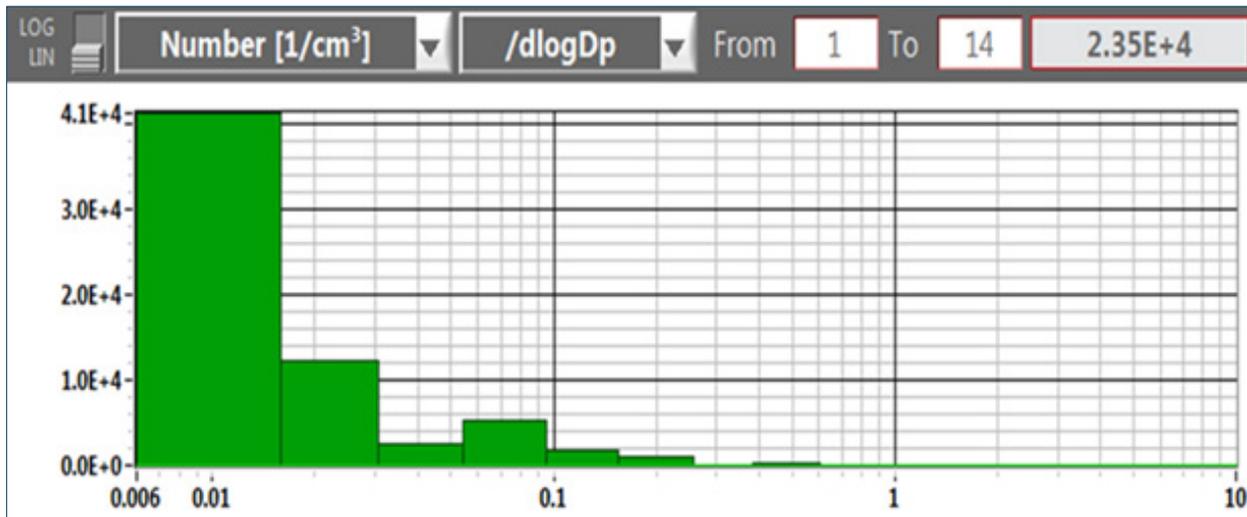


Figure 9. Screenshot of ELPI+ Results during Typical SSTU Operation

UT-Austin’s representative operated an FTIR spectrometer alongside the PDI to quantify the actual concentration of MEA present. Figure 10 provides results of the FTIR measurements taken prior to the baghouse installation (12/12/2015) and after the baghouse installation (10/10/2016). The data demonstrated that amine concentrations were significantly reduced after the baghouse installation.

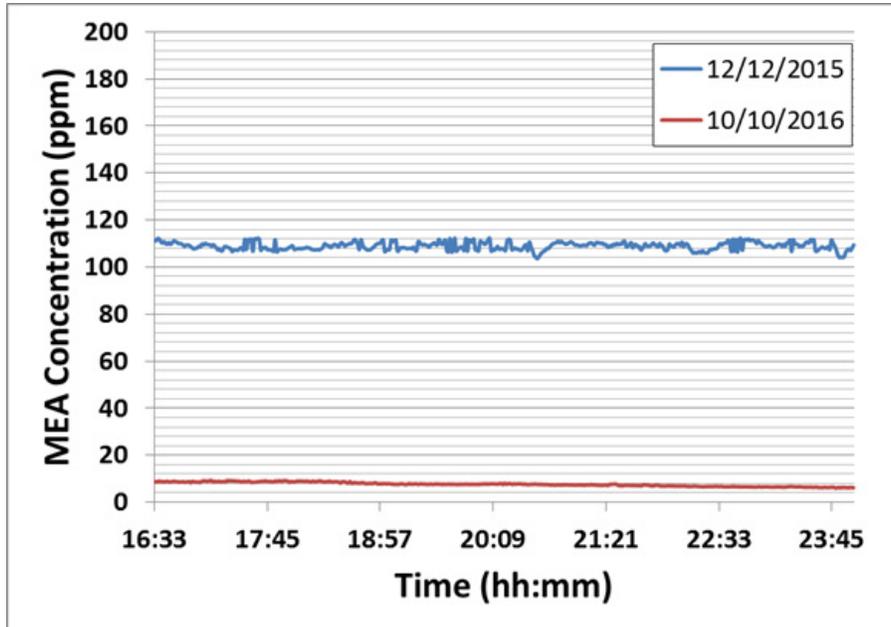


Figure 10. MEA Concentration in Treated Flue Gas Stream before and after Baghouse Installation as Sampled by the FTIR

Results of these and previous work on amine emissions studies at the NCCC were reported in three different papers.

- UT-Austin’s “Study of CO<sub>2</sub> Capture Solvent Emissions at the National Carbon Capture Center,” was posted on the NCCC website ([www.nationalcarboncapturecenter.com](http://www.nationalcarboncapturecenter.com)). This report focused on the results from the phase Doppler interferometer and Fourier transform infrared spectroscopy.
- Southern Research authored “Real-time Aerosol Measurements in Pilot Scale Coal Fired Post-Combustion CO<sub>2</sub> Capture,” published in the February 2017 issue of *Journal of Aerosol Science*. This paper reported the results generated from ELPI+ sampling and analysis.
- A third report, “Normal Smooth and Porous Sintered Collection Substrates for the ELPI+™ in Post-Combustion Aerosol Measurements” focused on the measurement differences between the uses of normal smooth and porous metal sintered substrates for ELPI+ operation. It will be published in the *Journal of Aerosol Science*.

## 2.6 CCSI<sup>2</sup> MEA Baseline in PSTU

NETL’s CCSI<sup>2</sup> has developed a computational toolset for modeling efforts to efficiently inform carbon capture R&D and reduce risks leading up to commercialization. Testing at the NCCC’s PSTU with MEA solvent was conducted in 2017 to provide data for further model validation. This test plan built on previous testing at the NCCC in December 2014, the results from which were used to validate the process model developed as part of the initial CCSI program.

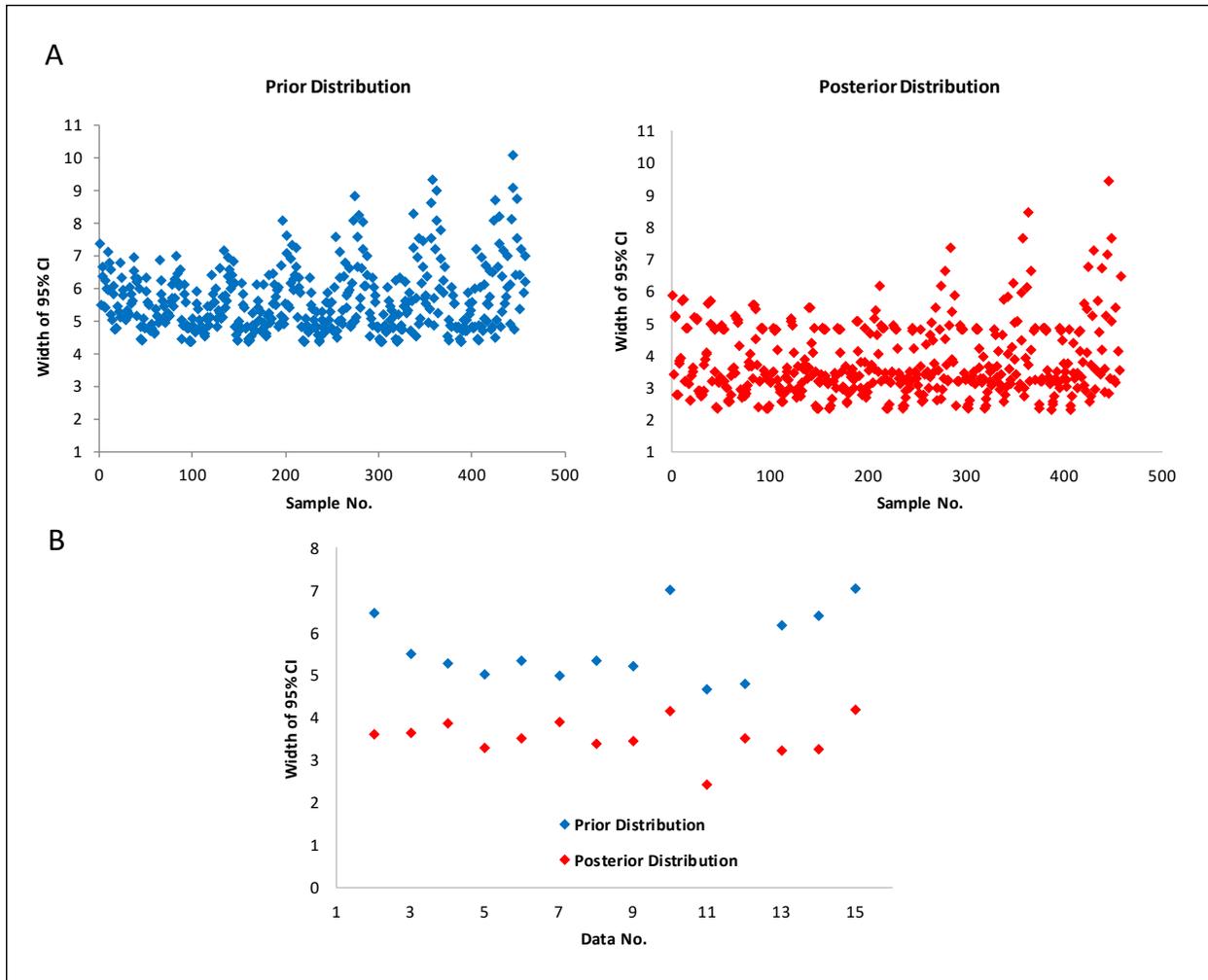
The 2017 campaign leveraged the existing model of the PSTU for an MEA system through a Bayesian experimental design. With this approach, the uncertainty in the process model prediction was estimated prior to test planning, then operating conditions were selected, and finally, the results were used to update the model parameters to reduce that uncertainty. The four major input variables and their ranges were:

- Lean solvent flowrate: 3,000 to 13,000 kg/hr
- Flue gas flowrate: 1,000 to 3,000 kg/hr
- Lean solvent loading: 0.1 to 0.35 mol CO<sub>2</sub>/mol MEA
- Flue gas CO<sub>2</sub> weight fraction: 0.125 to 0.175

These ranges were selected to provide realistic conditions and a CO<sub>2</sub> capture rate ranging from 50 to 95%. The MEA concentration was maintained at 30 wt% throughout the test campaign. The first 20 conditions were selected for 3-bed absorber operation with intercooling. The four input variables were modeled to calculate the expected CO<sub>2</sub> capture rate. Experimental data from the campaign was then used to update the process model parameters through an iterative process in the Bayesian inference methodology. These updated parameters were then fed into the Bayesian inference methodology to predict new model uncertainty values.

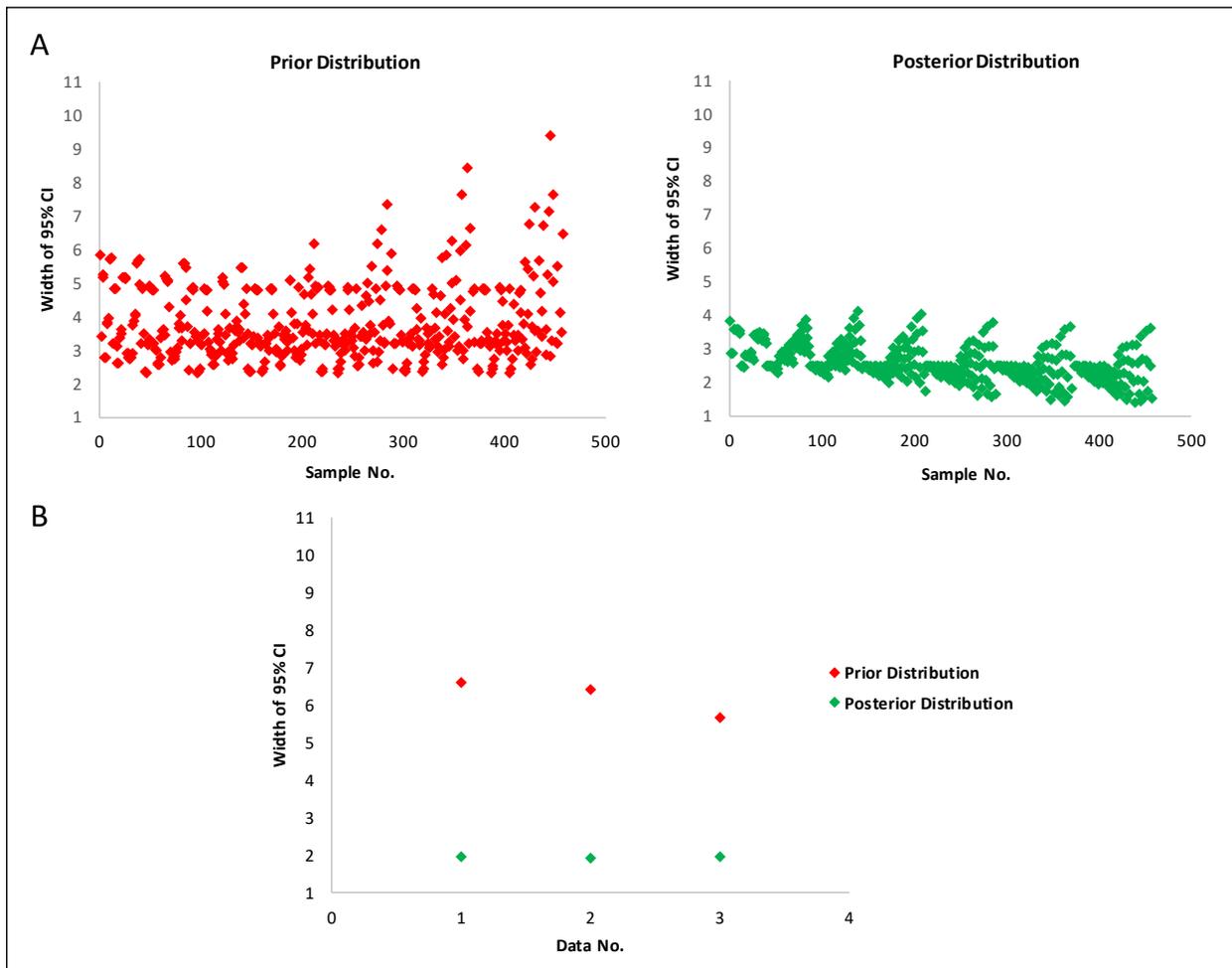
As shown in Figure 11, the first 20 test conditions resulted in a decrease in uncertainty. Confidence interval widths, as calculated by the surrogate absorber model, are shown for (A) a

grid of points spread throughout input space and for (B) points for which experimental data were collected.



**Figure 11. Initial Reduction in CO<sub>2</sub> Capture Rate Confidence Interval Width Resulting from CCSI<sup>2</sup> MEA Baseline Testing**

This process was then repeated for three additional conditions as time allowed and again resulted in improved confidence, clearly demonstrating the applicability of the Bayesian experimental design to planning a pilot plant test campaign. Figure 12 shows confidence interval widths, as calculated by the surrogate absorber model, for (A) a grid of points spread throughout input space and for (B) points from executed test runs.



**Figure 12. Secondary Reduction in CO<sub>2</sub> Capture Rate Confidence Interval Width Resulting from CCSI<sup>2</sup> MEA Baseline Testing**

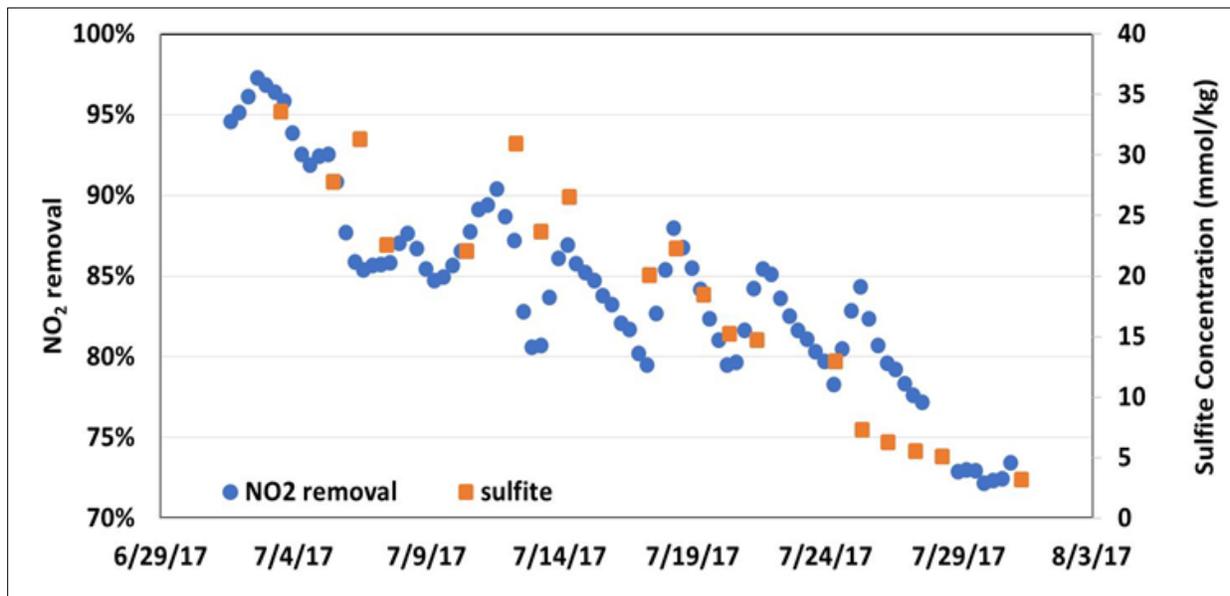
The effectiveness of the design of experiment methodology was clearly demonstrated for steady-state operations. Future projects will focus on developing a more efficient and computationally streamlined execution of the iterative Bayesian experimental design process. In addition to the steady-state work, two dynamic experimental design methodologies were successfully implemented, pseudo-random binary sequence and Schroeder-phased input. Work on dynamic data reconciliation is ongoing, and further work is planned to increase the usefulness of dynamic data. The CCSI<sup>2</sup> group continues to engage with technology developers and test centers to increase deployment of the computational toolset.

## 2.7 Trimeric/UT-Austin NO<sub>2</sub> Scrubbing

Trimeric and UT-Austin performed testing of a chemical process for removal of NO<sub>2</sub> from amine-based solvent systems in order to minimize solvent losses. Trimeric's application addresses the specific technical problem of how to prevent nitrosamine accumulation in the solvent system and minimize solvent oxidation. The presence of nitrosamines increases the cost

for capturing CO<sub>2</sub> and is an environmental concern. The process involved the use of a low-cost additive, thiosulfate, in an existing SO<sub>2</sub> pre-scrubber upstream of the PC4's Pilot Bay 3.

Because the flue gas used for testing is treated for NO<sub>x</sub> in an upstream selective catalytic reducer, an NO<sub>2</sub> additive system was installed to achieve a typical concentration for untreated flue gas. Figure 13 provides preliminary results, showing that NO<sub>2</sub> removal was strongly correlated to sulfite concentration in the pre-scrubber solution. The sulfite concentration was increased by adding thiosulfate. As sulfite concentration decreased during the test due to dilution from flue gas moisture condensation, the NO<sub>2</sub> removal rate decreased accordingly.

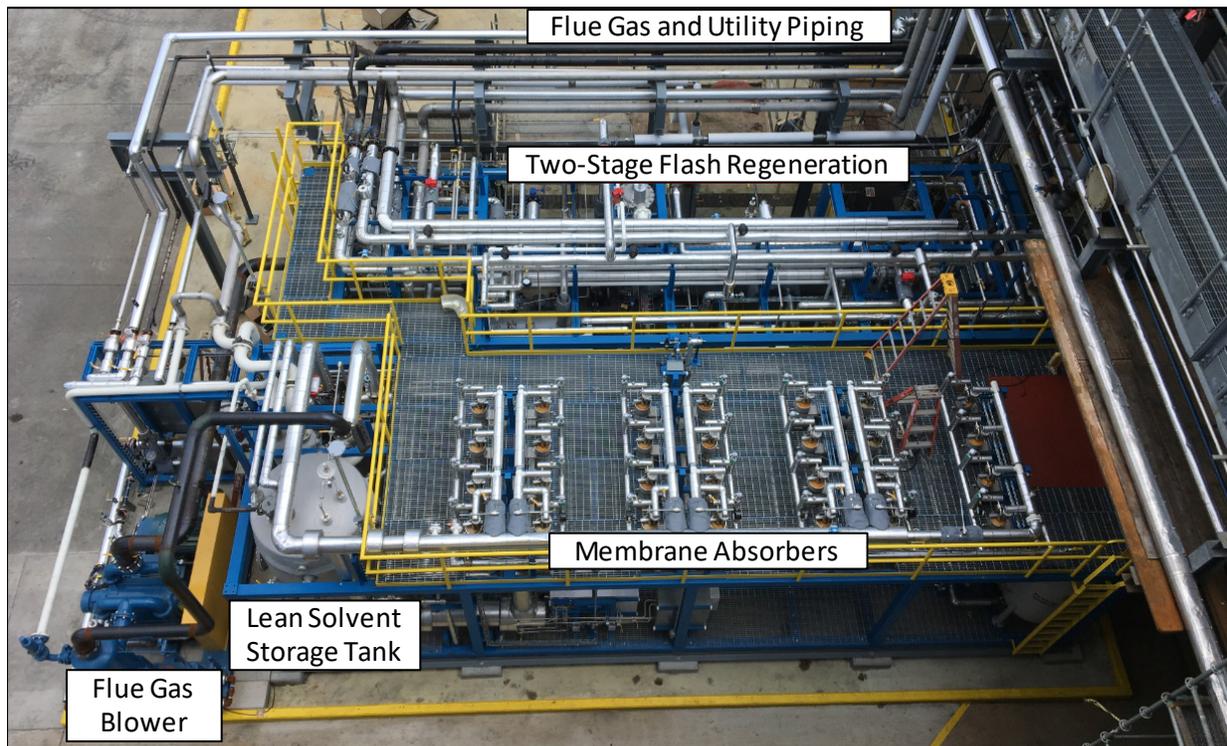


**Figure 13. NO<sub>2</sub> Removal and Sulfite Concentration in Pre-Scrubber during Trimeric/UT-Austin Testing**

Trimeric and UT-Austin personnel reviewed the data and will present initial findings at the 2017 NETL CO<sub>2</sub> Capture Technology Review Meeting in Pittsburgh, PA, in August. Trimeric is not currently planning for additional testing, although the UT-Austin group has been in discussions with industrial solvent suppliers regarding the combined scrubbing technology.

## 2.8 Gas Technology Institute Membrane Contactor

GTI, under DOE funding, is developing a hollow fiber gas-liquid membrane contactor to replace conventional packed bed columns to improve CO<sub>2</sub> absorption and desorption efficiency. It is a hybrid system that combines the advantages of membrane gas separation and solvent absorption mechanisms. Use of hollow fiber membrane configuration provides five to ten times higher gas/liquid contacting surface area than a conventional packed bed column, providing a significant capital cost reduction. After completing a small bench-scale project at another location, GTI is moving the technology forward with a small pilot-scale, 0.5 MW process installed at the PC4 in 2017. Figure 14 provides a photograph of the installed equipment.



**Figure 14. Gas Technology Institute Membrane Contactor Skids Installed at the PC4**

GTI conducted initial solvent testing with flue gas in late June and reported promising performance of 90% CO<sub>2</sub> capture with CO<sub>2</sub> purity greater than 97%. Parametric testing was underway during July, and testing was planned to continue through mid-August.

## 2.9 Future Post-Combustion Test Plans

Preparations were underway for testing in Budget Period Four during the PO-7 run at the PC4. The projects scheduled for testing are described below.

- AECOM and UT-Austin plan to demonstrate the AFS integrated with the PSTU, operating with piperazine solvent.
- TDA is developing a CO<sub>2</sub> capture process using dry, alkalized alumina sorbent, which is regenerable using low-pressure steam. The test will be conducted at a 0.5-MW scale.
- GTI will continue testing of the 0.5-MW hollow fiber gas-liquid membrane contactor.
- Building on previous testing at the site, NETL will resume bench-scale tests with hollow fiber membranes for identification of suitable materials.
- Air Liquide will begin their next phase of testing for the cold membrane process.

### 3.0 GASIFICATION

The NCCC gasification process, represented in Figure 15, features several key components of an Integrated Gasification Combined Cycle plant. These include high pressure solids feed systems; a Transport Gasifier; syngas coolers; a hot gas filter vessel, the Particulate Control Device; and continuous ash depressurization systems for ash cooling and removal. Gasification operation, which began in 1999, provides syngas for testing of gasification-related technologies in addition to testing of pre-combustion CO<sub>2</sub> capture technologies.

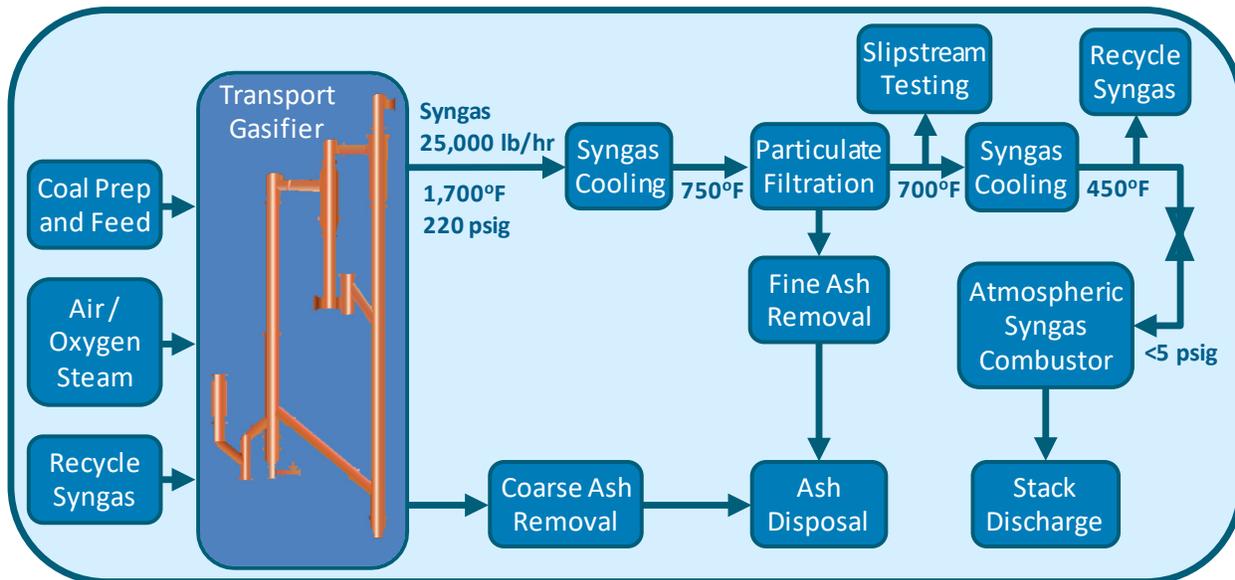


Figure 15. Schematic of NCCC Gasification Process

During the reporting period, the gasification process was operated for 900 hours during run G-5, supporting multiple technology developer projects, as described in the following sections. The average syngas composition and carbon conversion for the steady state periods are provided in Table 5.

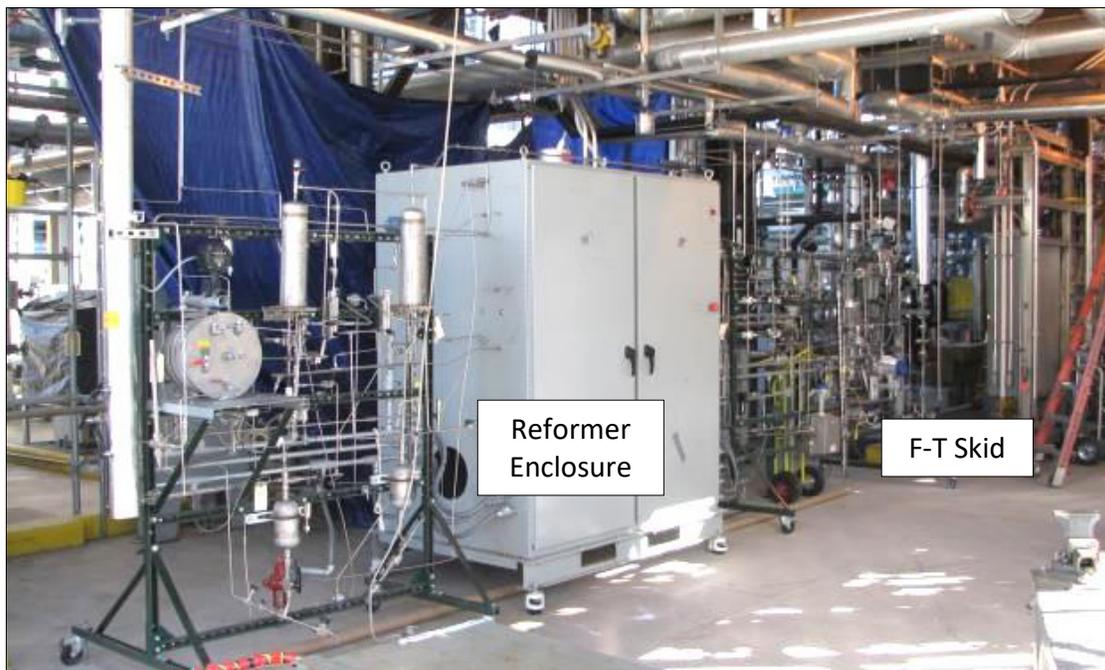
Table 5. Average Syngas Composition and Carbon Conversion for G-5 Steady State Periods

Syngas Component	Average Value
Carbon Monoxide, vol%	7.7
Hydrogen, vol%	6.1
Carbon Dioxide, vol %	8.2
Methane, vol%	0.9
Nitrogen, vol%	67.3
Water, vol%	9.2
Carbon Conversion, %	98.9

### 3.1 Southern Research Institute Fischer-Tropsch Catalyst and Steam Reformer

SR continued development of two separate technologies integral to improving the technical and economic viability of converting coal and/or biomass to jet fuel. The first technology, autothermal reforming, was evaluated by testing a high-temperature reforming catalyst in the presence of H<sub>2</sub>S and other syngas contaminants. The second technology, a novel Fischer-Tropsch process using Chevron's hybrid cobalt-zeolite catalyst to selectively produce wax-free jet fuel from syngas.

For G-5 testing, SR modified a lab-scale steam reformer skid for operation in a classified industrial environment. The reformer system consisted of two parallel flow paths: a 1-slp<sub>m</sub> stream routed to the reformer reactor vessel containing 10 grams of catalyst, and a 10-slp<sub>m</sub> stream used for syngas characterization using an online gas chromatograph. Figure 16 shows the reformer enclosure as well as the F-T reactor installed at the NCCC.



**Figure 16. Southern Research Fischer-Tropsch Catalyst and Steam Reformer Equipment**

SR successfully operated the reformer skid for 125 hours on syngas. Results indicated high conversion of methane (up to 90%) and near complete conversion of tar and ammonia in the presence of 380 ppm H<sub>2</sub>S. Testing demonstrated a strong effect of temperature on reforming catalyst performance, as a temperature drop of 50°C decreased methane conversion from 90% to 60%. However, the conversion rate quickly recovered when the temperature was again increased. SR also demonstrated a key goal during the experiments by controlling the hydrogen-to-carbon monoxide ratio exiting the reformer at 2-to-1 by manipulating the steam flow rate to the reactor. During the G-5 testing, catalyst performance did not indicate any damage by contaminants.

For testing of the F-T catalyst, SR modified a reactor system previously tested at the NCCC, increasing the reactor diameter from two inches to four inches. The previous testing demonstrated catalyst activity of greater than 0.7 grams of C5+ hydrocarbons per gram of catalyst per hour (gC5+/gcat/hr) and product selectivity of greater than 65% jet fuel. The modifications were made to further demonstrate scalability of the reactor heat removal technology. This work required redesigns of the feed, sampling, and cooling systems. As expected, temperature control was more difficult, but SR successfully tested the catalyst for 125 hours. SR's thermo-syphon system maintained reactor operating temperature along the axis to within  $\pm 5^{\circ}\text{C}$ . Results indicated similar catalyst productivity and liquid hydrocarbon selectivity but with higher jet fuel selectivity. Liquid hydrocarbon distribution measurements for G-5 samples indicated the jet fuel-range hydrocarbon selectivity was 75% with almost no hydrocarbons above C22 detected.

The most notable operational issue that occurred was an abrupt loss of carbon monoxide (CO) on the F-T process followed by a later abrupt restart of CO that caused a temperature runaway, damaging about 50% of the F-T catalyst. The operating team was required to develop new control strategies to operate without constant risk of temperature runaways.

### **3.2 Water-Gas Shift and COS Hydrolysis Catalysts**

Operation continued with a WGS catalyst that has been tested since 2011. Compared to conventional WGS catalysts, this catalyst is expected to have higher conversion rates at low temperatures (300 to 482°F) and improved resistance to degradation by sulfur. The G-5 testing confirmed the long-term durability for approximately 6,900 hours to date. The CO conversion rate was over 60% at a temperature of 480°F and a steam-to-CO ratio of 1.0, and was lower than 50% at temperatures ranging from 400 to 427°F and steam-to-CO ratios from 1.1 to 1.4. The conversion was slightly lower than that of previous testing, presumably due to degradation resulting from a thermal excursion (during which the catalyst was heated up to 1,500°F) occurring in the last test run.

A COS hydrolysis catalyst from the same developer was evaluated with parametric and long-term tests. This catalyst has been tested since 2013 for approximately 4,000 hours to date. During G-5, the COS conversion rate was stable, averaging about 50% at 570°F.

### **3.3 Ohio State University Syngas Chemical Looping**

OSU continued progress to demonstrate the high-pressure SCL process. This process is designed to convert syngas into separated hydrogen and CO<sub>2</sub> streams using a countercurrent moving bed reducer/oxidizer reactor system. After completing refractory repairs on the combustor vessel during the outage, a cold flow test verified proper fluidization in the combustor. During G-5, OSU completed system heat-up and operated the system with syngas feed while circulating oxygen carrier particles to prepare for operation with steam and begin hydrogen production. The SCL process operated with steam for a short period and produced hydrogen for the first time.

Syngas operation was achieved for 33 hours, including a continuous period of 15 hours. The typical gas profile measured at the SCL reducer outlet during steady-state operation is shown in

Figure 17. The majority of syngas was converted into CO<sub>2</sub>, with small amounts of carbon monoxide and hydrogen remaining unconverted.

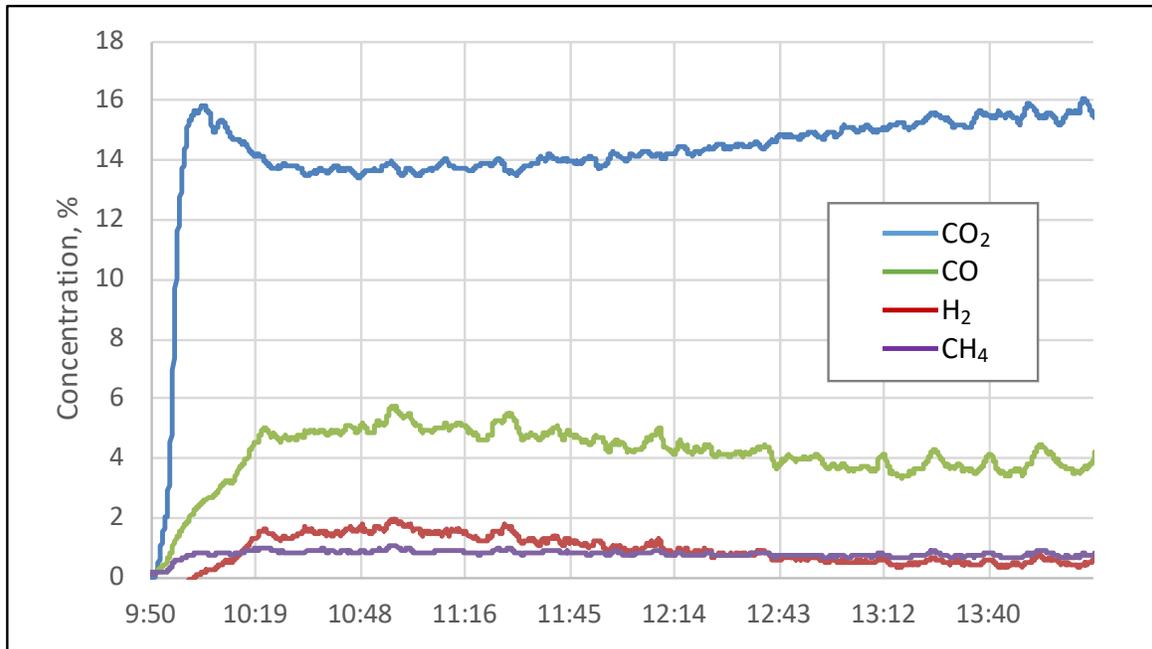


Figure 17. Typical SCL Reducer Outlet Gas Composition During Syngas Operation

The conversion rate of syngas was estimated using a carbon balance. Assuming that all the carbon in the syngas entering the reducer exits from the reducer outlet, the syngas conversion can be estimated from the concentrations of gas species,  $x_i$ , by the following formula:

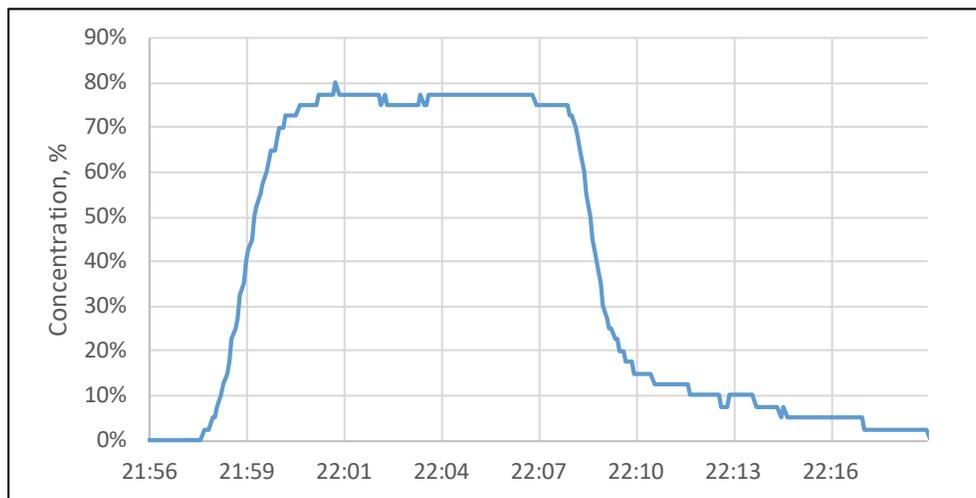
$$X_S = \frac{(n_{CO_2,out} - n_{CO_2,in}) + (n_{H_2,in} - n_{H_2,out})}{n_{CO,in} + n_{CH_4,in} + n_{H_2,in}} = \frac{\frac{\sum x_{C,in}}{\sum x_{C,out}} (x_{CO_2,out} - x_{H_2,out}) + x_{H_2,in} - x_{CO_2,in}}{x_{CO,in} + x_{CH_4,in} + x_{H_2,in}}$$

where  $n_i$  is the molar flow rate of compound  $i$ . The numerator of the above formula represents the amount of carbonaceous compounds and hydrogen that were converted in the reducer, while the denominator represents the amount of syngas that was fed into the reducer. Figure 18 shows the conversion of syngas in the reducer during the syngas operation represented in Figure 17. A syngas conversion of 70% was achieved. As the temperature continued to increase in the reducer as more syngas conversion led to higher temperatures in the combustor and more activation of the oxygen carrier, the syngas conversion continued to rise.



**Figure 18. Syngas Conversion in the SCL Reducer**

Hydrogen production from the oxidizer was also achieved during G-5 operation. Figure 19 provides the hydrogen concentration at the SCL oxidizer outlet during steam injection. The balance of the gas composition was nitrogen. An increase in hydrogen concentration was observed after steam injection to the oxidizer started. Carbonaceous compounds were not detected at the oxidizer, which indicated the absence of carbon deposition on the oxygen carriers in the SCL reducer as well as the proper operation of the non-mechanical gas sealing device that segregates the reducer and the oxidizer. The steam injection experiment confirmed that the SCL system is capable of converting syngas and steam into pure hydrogen.



**Figure 19. Hydrogen Concentration in SCL Oxidizer Outlet Gas**

Operation of the SCL pilot unit ended on April 30 due to a mechanical failure of the secondary cooler located at the outlet of the combustor. Damage of a heat exchanger tube caused leakage of air into the NCCC cooling water system, which led to the shutdown of the cooling water system and subsequently the gasifier system. OSU has developed plans to repair the heat exchanger and make other modifications for improved performance.

## 4.0 PRE-COMBUSTION CO<sub>2</sub> CAPTURE

The NCCC’s pre-combustion CO<sub>2</sub> capture program allows evaluation of solvents, sorbents, catalysts, membranes, and other emerging technologies at an appropriate scale with coal-derived syngas produced during gasification runs. Figure 20 is a schematic of the pre-combustion facilities, which include the Syngas Conditioning Unit and a separate unit for pilot-scale testing. The SCU uses up to 1,500 lb/hr and accommodates simultaneous testing of multiple technologies at different syngas conditions and flow rates. A variety of syngas treatment steps can be implemented to meet developer requirements such as sulfur removal, trace metal removal, WGS, and hydrocarbon treatment.

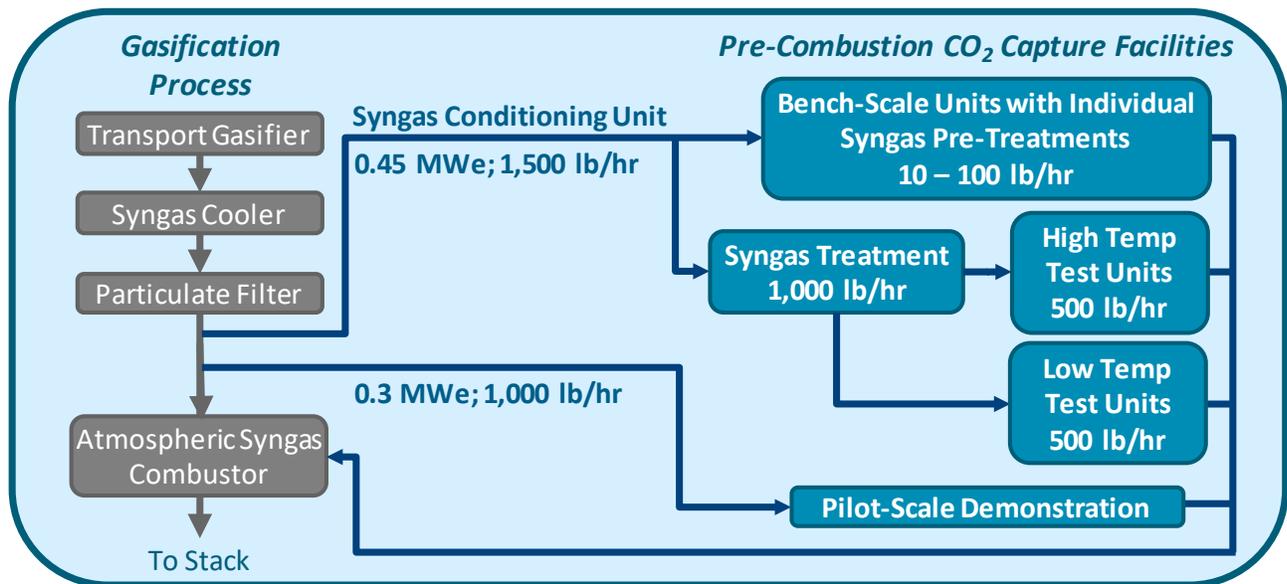
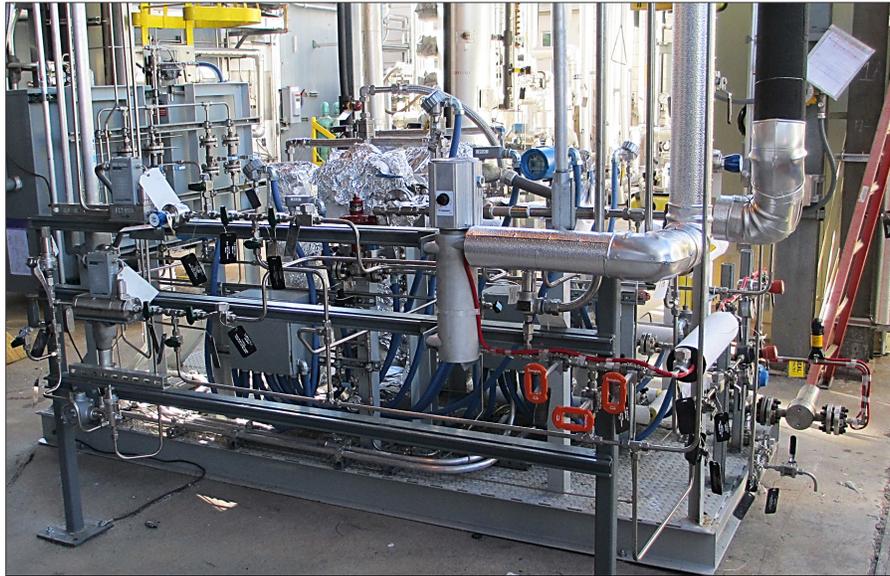


Figure 20. Schematic of Pre-Combustion CO<sub>2</sub> Capture Facilities

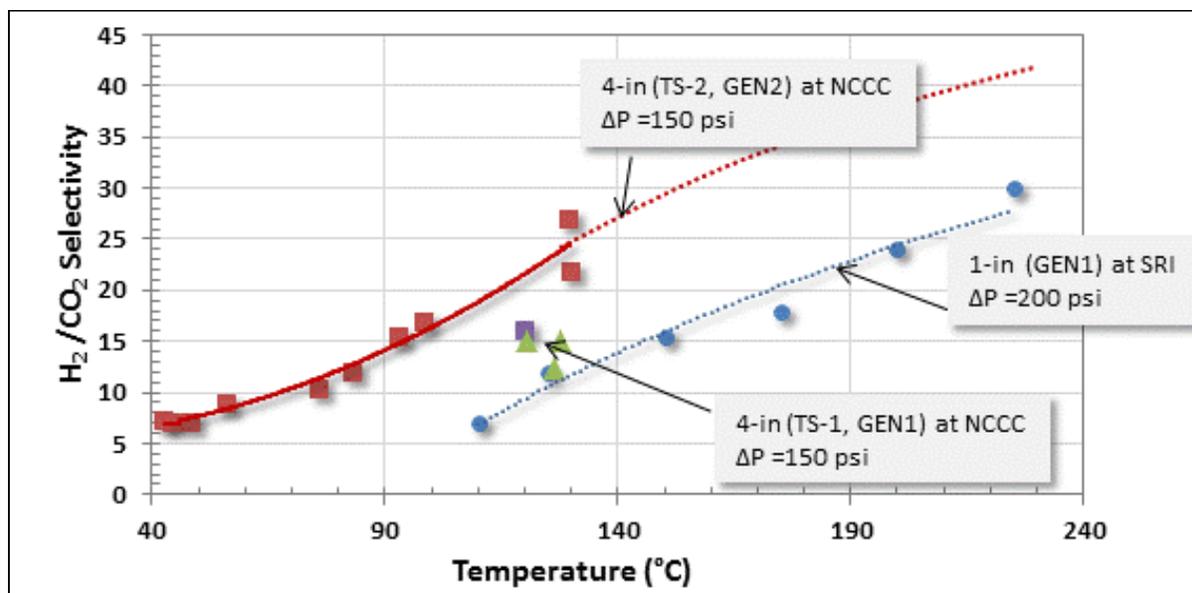
### 4.1 SRI International Polybenzimidazole Hydrogen Membranes

SRI conducted the first syngas testing with their PBI hydrogen membranes. The membrane skid installed at the NCCC is shown in Figure 21. Testing was performed with two modules, one with first generation (Gen-1) fibers, and one with second generation (Gen-2) fibers. Operation was at a 50-kWth scale using syngas and syngas supplemented with hydrogen and CO<sub>2</sub>. The Gen-1 module operated continuously for 500 hours at varying temperatures and pressures to evaluate its performance as a function of stage cut and different hydrogen and CO<sub>2</sub> concentrations. In parallel, SRI tested the Gen-2 module for 48 hours to measure its selectivity.



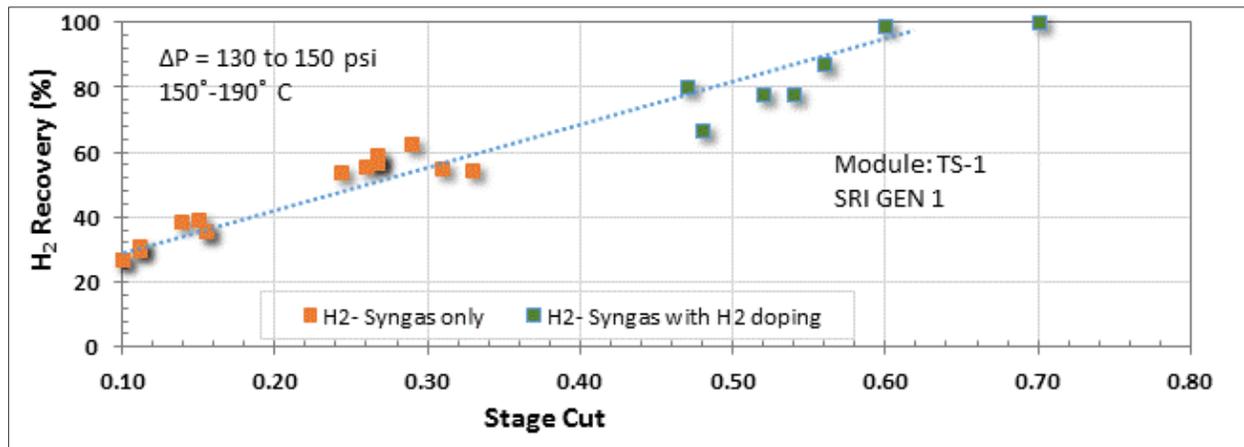
**Figure 21. SRI International PBI Membrane Skid**

Figure 22 shows that the hydrogen/CO<sub>2</sub> selectivity in the Gen-2 module increased with increasing temperature. This behavior is a unique property of the PBI hollow fiber membranes; conventional polymer membranes show the opposite effect. Figure 22 also shows the comparison of the selectivity data for the Gen-1 fibers and the data from the one-inch module testing at SRI with Gen-1 fibers. The 1-inch Gen-1 data showed that operating temperatures above 190°C (374°F) would be required to achieve a hydrogen/CO<sub>2</sub> selectivity of 25. In comparison, the Gen-2 module achieved a selectivity of 25 at temperatures below 140°C. The NCCC field test conditions confirmed that the Gen-2 fibers are superior.



**Figure 22. Comparison of Hydrogen/CO<sub>2</sub> Selectivity for GEN-1 and GEN-2 PBI Modules**

The module with Gen-1 fibers was tested with varying stage-cuts and supplied with either a syngas only feed or a syngas feed augmented with additional hydrogen and CO<sub>2</sub>. The overall observed performance data is given in Figure 23. As expected, the hydrogen recovery was greater (about 99%) at the higher stage cut (0.6), while the CO<sub>2</sub> recovery was higher (greater than 90%) at the lower stage cut (0.4). The data also showed that, at temperatures above 150°C (302°F), the hydrogen recovery depended mostly on the operating stage cut. The modules tested were constructed with a dead-end design, i.e., fiber shell-side gas feed with one end of fiber bore-side sealed in the potted module. SRI expects much improved performance for the membranes potted with both bore-side ends open to allow a bore-side flow-through configuration enabling the use of permeate sweep gas to further optimize hydrogen recovery and CO<sub>2</sub> capture.

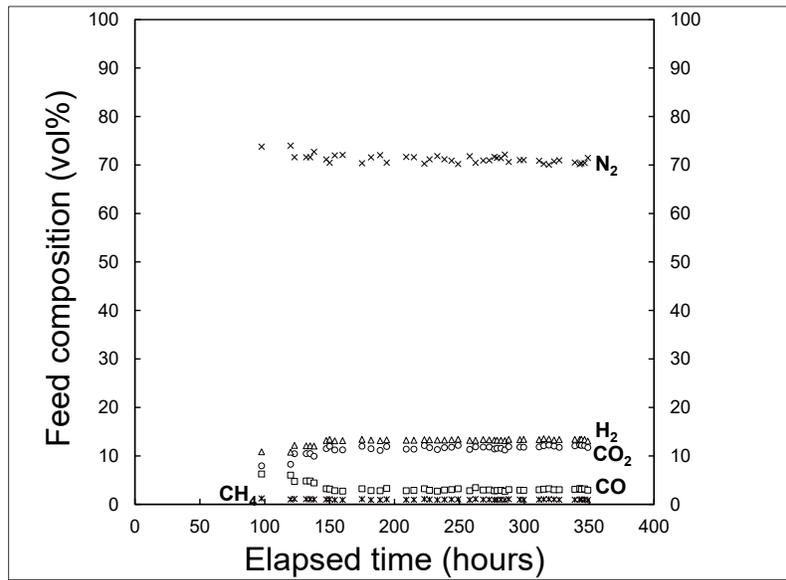


**Figure 23. Hydrogen Recovery of PBI Membrane with Varying Stage Cuts**

SRI will use the test data to update an economic analysis of the technology. The analysis will define how the high-temperature hollow-fiber PBI membrane process concept would be incorporated into a nominal 550-MWe gasification-based power plant with CCUS, using as the base case IGCC process based on a GE-oxygen-blown gasifier with Selexol-based CO<sub>2</sub> removal. This work will be performed in collaboration with the Electric Power Research Institute. Future test plans include conducting a longer test campaign with Gen-2 modules to evaluate the stability of epoxy fiber potting at higher temperatures.

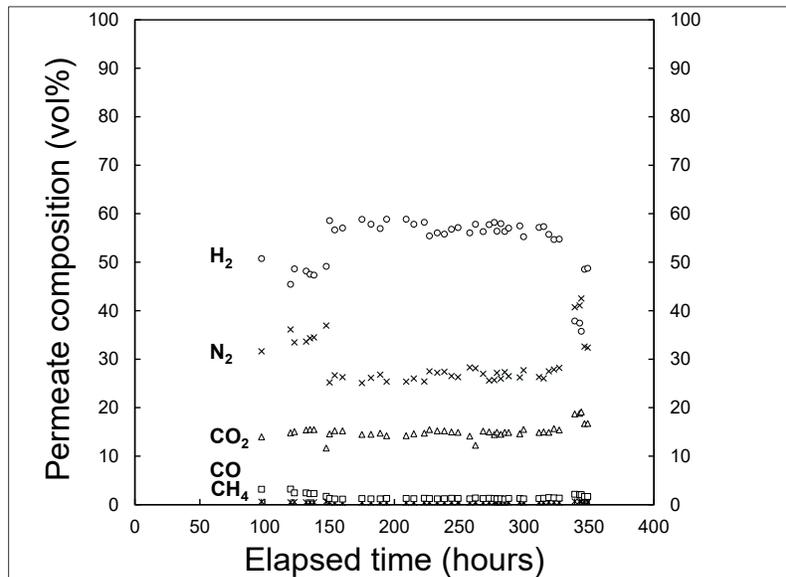
## 4.2 Membrane Technology & Research Proteus Membranes

MTR continued development of Proteus hydrogen membranes, testing a single 4-inch diameter membrane module for the duration of the G-5 run. The module was previously tested for approximately 300 hours during the G-3/G-4 run in 2016 and was made with an improved glue and spacer configuration on the feed side compared to previous modules tested at NCCC. For the duration of testing on the 50 lb/hr unit, the temperature of the syngas entering the module vessel was maintained at 110°C (230°F), and the syngas feed pressure was kept constant at 170 psig. No hydrogen enrichment was utilized during G-5 testing. The feed compositions for the module is shown in Figure 24. The feed and permeate concentrations were not available for the first 100 hours of testing due to inconsistent or incomplete GC data.



**Figure 24. Syngas Feed Composition for MTR's Four-Inch Membrane Module**

The permeate concentrations are given in Figure 25 which demonstrate how sensitive the Proteus membrane is to the hydrogen partial pressure driving force. Between 100 and 150 hours of run time, the hydrogen permeate concentration was about 50% before rising to 60% for most of the remainder of the run.



**Figure 25. Permeate Stream Composition for MTR's Four-Inch Membrane Module**

The reason for the difference in permeate hydrogen concentration is related to the hydrogen content in the feed syngas, which varied based on the WGS conversion rate of the syngas in a reactor upstream of the MTR membrane skid. Prior to 150 hours of runtime, the average hydrogen concentration in the syngas feed was 9.6%, while after 150 hours, the average was

11.7%. The influence of the WGS conversion rate can also be seen in the concentrations of CO (5.2% vs 3.0%) or CO<sub>2</sub> (11.6% vs. 13.3%) in the feed syngas before and after 150 hours of runtime.

Between 340 hours and the end of the run, the permeate hydrogen concentration dropped considerably while the feed hydrogen content was virtually unchanged. The drop in permeate hydrogen concentration was due to an increase in the permeate pressure, which lowered the hydrogen partial pressure driving force across the membrane by 85%. The permeate pressure increase was thought to be caused by the accumulation of debris in the permeate piping.

The module showed hydrogen enrichment (defined as the permeate hydrogen concentration divided by the feed hydrogen concentration) of about 5 for both the G-5 run and for the previous run. The consistent hydrogen enrichment value attests to the high quality of the module and absence of deterioration over the two runs.

### 4.3 Media & Process Technology Palladium-Based Hydrogen Membranes

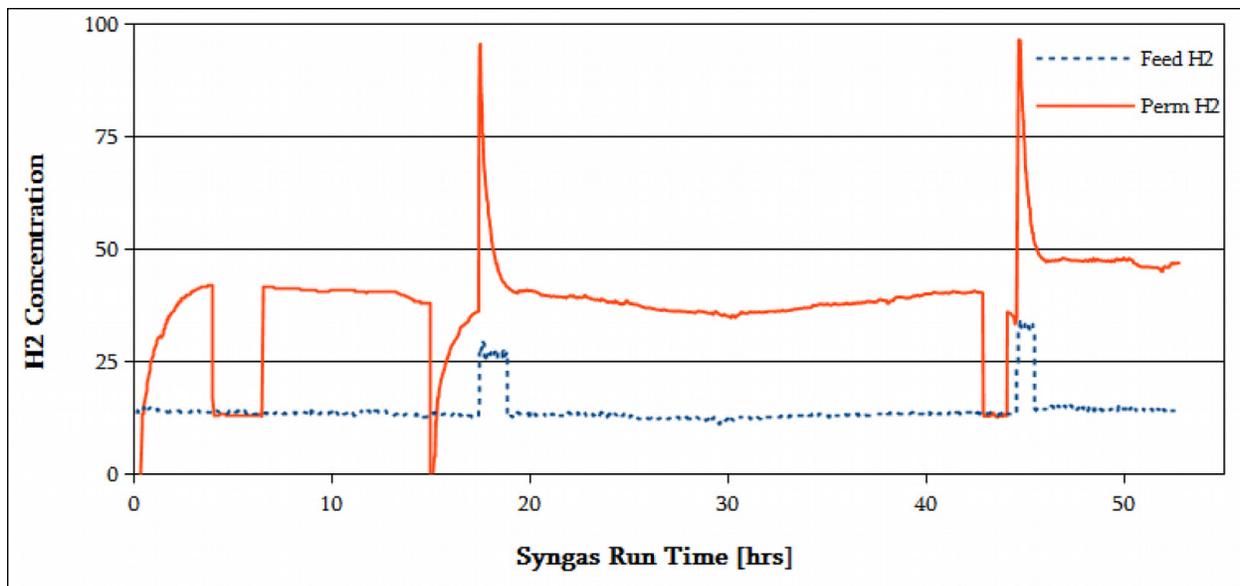
In previous testing, MPT produced hydrogen with greater than 99% purity using the CMS along with a downstream single-tube palladium membrane. For run G-5, MPT scaled up the palladium membrane to a multi-tube bundle and operated it independently. The test objectives were to evaluate the physical integrity of the palladium membrane bundle, determine the impact of syngas contaminants in the presence of tar-like species, and assess the membrane's ability to be regenerated. To achieve these objectives, MPT used as the feed gas syngas that was pre-treated with water-gas shifting and desulfurization, but not treated to remove tars. Three membrane bundles were tested, each consisting of 12 tubes, which were 12 inches in length, as shown in Figure 26.



Figure 26. MPT Membrane Bundles and Housing Units

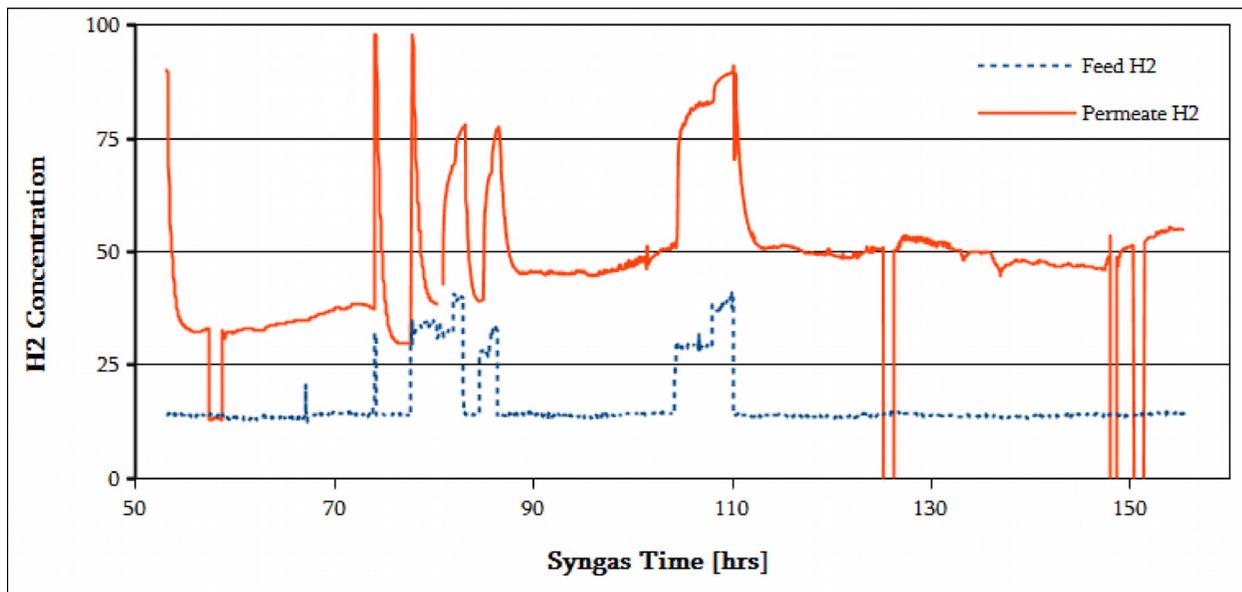
Prior to operation, modifications were made to the system to allow in-situ oxidation and regeneration of the membranes, which comprised brief exposure to air at 310°C (590°F). The G-5 testing included 156 hours of syngas permeation run time and 176 hours of membrane regeneration. Each bundle was oxidized in-situ before syngas feed was started.

Bundle A was a relatively low selectivity bundle intended for initial testing while proving out the system prior to testing higher quality bundles. Figure 27 plots the overall hydrogen separation performance, which was low for a palladium-based membrane. At hours 5 through 7 and 42, the bundle was bypassed. Following in-situ oxidation at hour 44, the performance improved slightly, although the hydrogen purity remained below 50%. Pure hydrogen permeance values taken intermittently during the test period confirm very low hydrogen permeation rates in the range of 300 to 550 gas permeation units (GPUs).



**Figure 27. Hydrogen Concentration of Feed and Permeate Streams of MPT’s Membrane Bundle A**

Bundle B was a higher quality bundle which showed hydrogen permeance values between 3,200 and 4,000 GPU and a separation factor for hydrogen/nitrogen of approximately 1,800 prior to G-5 testing. Figure 28 plots the overall gas separation performance of this bundle. The initial pure hydrogen permeance ranged from 350 to 500 GPU, indicating that the initial in-situ oxidation did not fully remove all the in-system tar and any other contaminants on the membrane surfaces. In-situ oxidation at hours 74, 80, and 85 yielded modest improvements in pure hydrogen permeance (up to 700 GPU) and slight improvement in syngas separation performance.



**Figure 28. Hydrogen Concentration of Feed and Permeate Streams of MPT’s Membrane Bundle B**

Testing of the third bundle, Bundle C, was limited by the unexpected early shut down of the gasifier, and thus not enough data was generated for comparison of this bundle with the others. Prior to testing, the hydrogen permeances of Bundle C ranged from 2,750 to 3,500 GPU, and during G-5 operation, the permeance ranged from 400 to 625 GPU.

Though in-situ regeneration was attempted for restoration of membrane activity, the presence of tar in the syngas and residual tar in the system prevented measurements of true hydrogen permeance. However, MPT demonstrated that the permeance could be restored in the lab with air treatment at raised temperatures. Following the G-5 testing, three membranes were cut from Bundles A and B for this regeneration testing. Table 6 lists the hydrogen permeance values at the beginning and end of the tests. The regenerated membranes maintained their original permeance for an extended period in the lab.

**Table 6. Hydrogen Permeance of MPT’s Palladium Membranes during Lab Regeneration**

Single Tube Membrane ID	Hydrogen Permeance, GPU		
	Beginning of Regeneration Test	End of Regeneration Test	
		310°C	310°C
Bundle A -1	912	2,900	
Bundle A -2	885		3,653
Bundle A -3	786		4,401
Bundle B -1	785	4,562	5,265
Bundle B -2	863	3,450	3,782
Bundle B -3	1535	4,198	
Bundle B-4	867	3,535	

#### 4.4 TDA Research 0.1-MW CO<sub>2</sub> Sorbent System

TDA Research is developing a sorbent-based pre-combustion carbon capture technology for integrated gasification combined cycle power plants. One of the major goals of the work is to assess the techno-economic viability of the new technology by carrying out evaluations in a pilot-scale unit using coal-derived syngas. TDA's test unit consists of eight beds and the needed subsystems to support the operation of the full pressure swing adsorption cycle. The sorbent test skid was designed to treat up to 2,000 slpm of raw syngas. The pilot-scale evaluation system also includes a gas conditioning skid, consisting of desulfurization sorbent beds, water-gas-shift reactors (both high temperature and low temperature) and a trace contaminant removal bed (mainly for mercury and arsenic). Figure 29 provides a photograph of the two skids installed at the NCCC.



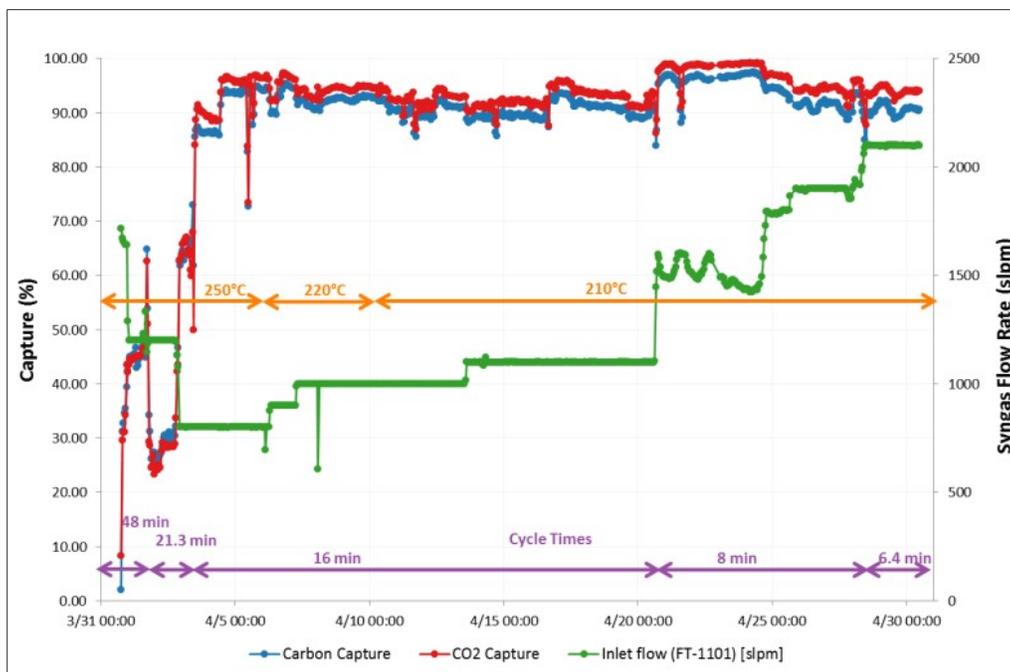
**Figure 29. TDA Research CO<sub>2</sub> Sorbent Test Skids**

For the G-5 testing, TDA varied the main parameters along the range of operation shown in Table 7. For these parameters, 75 unique combinations were tested. The robust control system allowed for wide range of testing, which permitted fine tuning of the performance for each of the cycle sequences. TDA achieved 740 hours of testing.

**Table 7. Operating Parameters for TDA Sorbent Process**

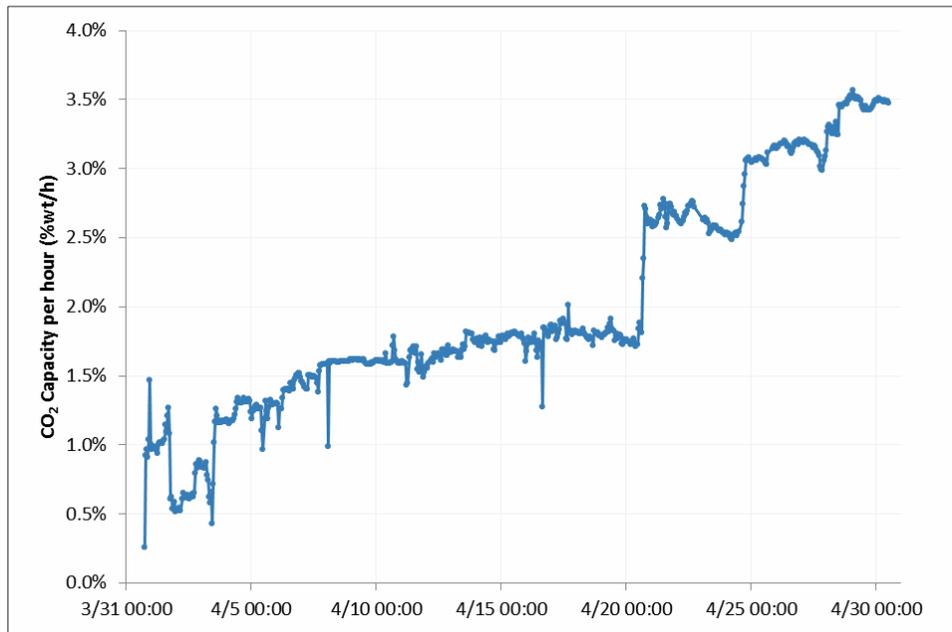
Condition	Minimum	Maximum
Regeneration Pressure, psig	15	30
Incoming Syngas Flow, slpm	800	2,100
Adsorption Pressure, psig	140	190
Regeneration Steam Flow, slpm	200	1,200
Recycle Loop Operation	Off	On
Number of Beds in Parallel Flow	1	2
CO <sub>2</sub> Sorbent Bed Temperature, °C (°F)	200 (392)	250 (482)
Cycle Time, min	6.4	48

Figure 30 shows the carbon and CO<sub>2</sub> capture results throughout the testing. It also includes the major process changes that occurred. Except for the first few days of testing, the CO<sub>2</sub> removal efficiency exceeded 90%. When the total cycle time was reduced to eight minutes, the CO<sub>2</sub> removal efficiency exceeded 99%.



**Figure 30. Carbon and CO<sub>2</sub> Capture Results for TDA Sorbent Technology**

Figure 31 shows the working capacity achieved by the sorbent (on a weight basis). As indicated in the figure, as the test progressed and the optimum operating conditions were identified, the CO<sub>2</sub> capacity of the sorbent was improved.



**Figure 31. Working Capacity of the TDA Sorbent over Time**

Table 8 gives a comparison of performance between the design and actual conditions at NCCC. Testing showed that the system, as designed, could provide the desired CO<sub>2</sub> removal. Additionally, at the end of the test, the system treated more than twice the design flow while capturing 90% of the carbon. Testing at the NCCC provided TDA with the opportunity to identify the needed, minor changes prior to further testing.

**Table 8. Comparison of Design and Actual Conditions for TDA Testing**

Condition	Design	Actual	
Syngas Flow into Conditioning Skid, scfm	43	39	53
Syngas Flow into CO <sub>2</sub> Sorbent Skid, scfm	48	42	57
Steam Added for WGS, scfm	4.1	2.7	4.3
CO <sub>2</sub> Captured, kg/hr	25	20.6	29.6
Cycle time, min	16	16	8
CO <sub>2</sub> Partial Pressure, psi	29.0	28.8	28.8
Bed Utilization, g CO <sub>2</sub> /L/hr	15.9	12.9	18.5

TDA plans to incorporate minor modifications based on G-5 operation, and TDA will ship the skid to China’s Sinopec group for further demonstration.

## 5.0 CONCLUSIONS AND LESSONS LEARNED

### 5.1 Post-Combustion

The post-combustion runs conducted in BP3 included:

- PO-5, beginning in Budget Period 2, from May 18, 2016, through February 27, 2017
- PO-6, occurring from June 12, 2017, and continuing into Budget Period 4 (through mid-August 2017)

Conclusions and lessons learned from the test runs are listed below.

#### ***Air Liquide Cold Membrane***

Air Liquide continued testing of its 0.3-MW cold membrane process and evaluation of membrane materials. Operation included parametric tests on both 6-inch and 12-inch PI-1 membrane bundles and a 1-inch PI-2 membrane bundle. Major findings are provided below.

- As demonstrated by the CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity values of the PI-1 bundles, the 6-inch configuration is the most ideal of the three.
- The 1-inch PI-2 bundle showed superior CO<sub>2</sub> permeance (more than 6.5 times higher) than the PI-1 bundles. However, the CO<sub>2</sub>/N<sub>2</sub> selectivity for the PI-2 bundle was lower than all of the PI-1 bundles. The data suggested further improvement could be realized with scale up of the PI-2 bundle to 6 or 12 inches.
- Membrane bundle performance improved as the temperature decreased from -45°C (-49°F) down to -50°C (-58°F).
- Arrangement with two bundles in series did not show superior performances compared to single bundles.
- Testing under various flue gas feed pressures, permeate pressures, and sweep gas flow rates showed that the 6-inch bundle was superior and exhibited the most ideal counter-current flow behavior.
- Analysis of flue gas contaminants confirmed that impurities such as mercury, selenium, and NO<sub>x</sub> were reduced to levels below detection limits in the membrane feed due to their removal in the pretreatment condensates, dryer bed, and activated alumina bed.

Further testing is planned in late 2017 under a new DOE contract, with the focus on scale-up with the PI-2 material and commercial bundle testing.

#### ***GE Global Research Aminosilicone Solvent and Desorber***

GE Global tested its GAP-1 solvent in the PSTU for over 900 hours of operation using two desorption designs: GE's CSTR, and the PSTU regenerator column. Key findings were:

- Several issues were encountered during early operation of the integrated PSTU/CSTR system, including the tendency of solvent foaming in the CSTR, which resulted in solvent carryover and loss. Through experimentation, it was determined that foaming and solvent carryover were minimized by maintaining the water concentration at 5% or less while operating the CSTR at 7 psig.
- Operation with the CSTR achieved 95% CO<sub>2</sub> capture efficiency at a solvent-to-CO<sub>2</sub> molar ratio of 4 and a desorption temperature of 110°C (230°F).
- The PSTU regeneration column was found to be more robust in regard to solvent entrainment. Under stoichiometric conditions, CO<sub>2</sub> capture efficiency was between 90 and 95% at a solvent-to-CO<sub>2</sub> molar ratio of 0.5, a desorption temperature of 235°F, a pressure of 2 psig, and a water content of 19 wt%.
- The GAP-1 solvent exhibited a 25% increased working capacity, and 10% reduction in specific steam duty as compared to MEA, at 5.5°C (10°F) lower desorption temperature.
- At \$48/ton CO<sub>2</sub> removed, the estimated first-year cost for CO<sub>2</sub> removal for the aminosilicone-based carbon capture process using a steam stripper column was 20% lower than for MEA, primarily due to lower overall capital cost. The estimated cost of CO<sub>2</sub> capture using the CSTR was higher due to higher solvent make-up requirements.

### ***CCSI<sup>2</sup>MEA Baseline Testing in the PSTU***

The PSTU was operated with MEA baseline solvent in support of the CCSI<sup>2</sup>, the second phase of the CCSI. The test campaign built on previous testing, using a Bayesian experimental design to reduce uncertainty in the carbon capture model. The effectiveness of the experimental design methodology was clearly demonstrated for steady-state operations. Future projects will focus on developing a more efficient and computationally streamlined execution of the iterative Bayesian experimental design process. In addition to the steady-state work, two dynamic experimental design methodologies were successfully implemented, pseudo-random binary sequence and Schroeder-phased input. Work on dynamic data reconciliation is ongoing, and further work is planned to increase the usefulness of dynamic data. The CCSI<sup>2</sup> group continues to engage with technology developers and test centers to increase deployment of the computational toolset.

### ***Slipstream Solvent Test Unit***

Based on the previous commissioning of the SSTU, several modifications were made to improve operating performance. Further operation with MEA during run PO-5 demonstrated more stable operations, and testing in run PO-6 was underway to identify optimal conditions. Lessons learned from operation in BP3 were:

- The CO<sub>2</sub> recovery rate improved dramatically with the addition of a blower upstream of the absorber, as opposed to the original as-delivered unit design containing a downstream blower.
- A positive pressure profile and its steady control are paramount for stable carbon capture in amine-based systems, and improvements to the backpressure control system were required for the completion of steady-state testing.

- A focus on instrumentation types, their installation, and the ability to evaluate their function with cross-checks incorporated into the system design are critical for ensuring data accuracy. The review of the as-provided pitot-style flow meters revealed improper installation that yielded erratic measurements and required redesign and replacement with V-cone style flow elements.

### ***Amine Emissions Studies***

Solvent emissions measurements were taken during operation of the SSTU with MEA solvent to further quantify the effects of an upstream baghouse on flue gas aerosols and subsequently on emissions. In addition to the ELPI+ measurements for aerosol size and count, a phase Doppler interferometer and an FTIR were used on the SSTU treated flue gas stream.

- A significant drop in the flue gas aerosol count resulted from the baghouse removal of the majority of the flue gas SO<sub>3</sub>.
- The ELPI+ data showed a shift in particle size distribution and particle count, but the PDI was unable to provide any indication of aerosols present because the particle sizes were below the detectable range of the instrument.
- Data from the ELPI+ showed that the majority of particles were below 0.1 microns in diameter, which is below the detection limit of the PDI.
- Results from the FTIR operation showed that the concentration of amine in the SSTU outlet were significantly reduced.
- Results of these and previous work on amine emissions studies at the NCCC were reported in three different papers.

### ***NETL Membranes***

As a continuation of previous testing in 2015, NETL operated its post-combustion membrane skid to identify materials with acceptable CO<sub>2</sub> separation performance in the presence of water vapor and minor contaminants. Due to software issues and equipment deficiencies, however, the testing did not produce useful data. Because the gas chromatograph had required extensive maintenance throughout testing, and because it performed reliably for only short periods, NETL began efforts to procure a new Siemens Maxum II GC, as recommended by NCCC. NETL temporarily used a GC borrowed from the NCCC gasification process, but found that it did not provide the full suite of data required. NETL plans for additional testing in 2018.

### ***Trimeric/UT-Austin NO<sub>2</sub> Scrubbing***

Trimeric and the UT-Austin completed testing of a chemical process for removal of NO<sub>2</sub> from amine-based solvent systems in order to minimize solvent losses. The process involves the use of low-cost additives in an existing SO<sub>2</sub> pre-scrubber. Results showed that:

- NO<sub>2</sub> removal was strongly correlated to sulfite concentration in the pre-scrubber solution. The sulfite concentration was increased by adding thiosulfate.

- As sulfite concentration decreased during the test due to dilution from flue gas moisture condensation, the NO<sub>2</sub> removal rate decreased accordingly.

### ***Gas Technology Institute Hollow Fiber Membrane Contactor***

GTI completed installation and began testing of a hollow fiber gas-liquid membrane contactor, which is a hybrid system combining the advantages of membrane gas separation and solvent absorption mechanisms. Initial testing demonstrated 90% CO<sub>2</sub> capture and CO<sub>2</sub> product purity greater than 97%. Testing was planned to continue through mid-August 2017.

## **5.2 Gasification**

The gasification process operated in run G-5 for 900 hours. The runs allowed for more than 1,800 hours of gasification technology developer testing. Operation was stable, with high carbon conversions and consistent quality syngas for use in gasification and pre-combustion tests.

### ***Southern Research Fischer-Tropsch Catalyst and Steam Reformer***

SR tested two technologies integral to improving the technical and economic viability of converting coal and/or biomass to jet fuel. The first technology is a F-T process using Chevron's hybrid cobalt-zeolite F-T catalyst to selectively produce jet fuel from syngas. The second technology, autothermal reforming, was evaluated by testing a high-temperature reforming catalyst in the presence of H<sub>2</sub>S and other syngas contaminants.

- SR incorporated a four-fold scale-up of the F-T reactor and tested the steam reformer for the first time.
- The F-T catalyst testing produced results similar to previous testing in regard to catalyst productivity and liquid hydrocarbon selectivity, but the jet fuel selectivity was higher, at 75%.
- A temperature excursion occurred in the F-T reactor as a result of an interruption and restart of the CO feed. SR compensated for the damage caused to a portion of the catalyst by adjusting the flow rate. The operating team was required to develop new control strategies to operate without constant risk of temperature runaways.
- The reformer demonstrated up to 90% conversion of methane and nearly complete conversion of tars in the presence of approximately 380 ppm of H<sub>2</sub>S.
- Testing demonstrated a strong effect of temperature on reforming catalyst performance, as a temperature drop of 50°C decreased methane conversion from 90% to 60%. However, the conversion rate quickly recovered when the temperature was again increased.
- SR also demonstrated a key goal during the experiments by controlling the hydrogen-to-carbon monoxide ratio exiting the reformer at 2-to-1 by manipulating the steam flow rate to the reactor.

### ***WGS and COS Hydrolysis Catalysts***

Operation of WGS and COS hydrolysis catalysts continued with parametric and long-term testing.

- Testing confirmed the long-term durability of the water-gas shift catalyst, which had accumulated 6,900 hours at the end of the G-5 run. The CO conversion rate was over 60% at a temperature of 480°F and a steam-to-CO ratio of 1.0, and was lower than 50% at temperatures ranging from 400 to 427°F and steam-to-CO ratios from 1.1 to 1.4. The conversion was slightly lower than that of previous testing, presumably due to degradation resulting from a thermal excursion (during which the catalyst was heated up to 1,500°F) occurring in the last test run.
- The COS hydrolysis catalyst was stable, averaging about 50% COS conversion at 570°F, and having accumulated about 4,000 hours.

### ***OSU Syngas Chemical Looping***

OSU continued progress to demonstrate the high-pressure SCL process. After completing refractory repairs on the combustor vessel during the outage, OSU completed system heat-up and operated the system with syngas feed while circulating oxygen carrier particles to prepare for operation with steam and begin hydrogen production. Highlights of operation were:

- Syngas operation was achieved for 33 hours, including a continuous period of 15 hours. The majority of syngas was converted into CO<sub>2</sub>, with small amounts of carbon monoxide and hydrogen remaining unconverted.
- A syngas conversion of 70% was achieved. As the temperature continued to increase in the reducer as more syngas conversion led to higher temperatures in the combustor and more activation of the oxygen carrier, the syngas conversion continued to rise.
- The process produced hydrogen for the first time. Steam condensation in the secondary cooler prevented extended operations for hydrogen generation.
- The steam injection experiment confirmed that the SCL system is capable of converting syngas and steam into pure hydrogen.
- Carbonaceous compounds were not detected at the oxidizer, which indicated the absence of carbon deposition on the oxygen carriers in the SCL reducer as well as the proper operation of the non-mechanical gas sealing device that segregates the reducer and the oxidizer.

## **5.3 Pre-Combustion**

Pre-combustion CO<sub>2</sub> capture operation during the G-5 run comprised over 1,700 hours of technology developer testing involving three types of hydrogen membranes and a solid sorbent technology.

### ***SRI PBI Hydrogen Membranes***

SRI conducted the first syngas testing of a hydrogen membrane fabricated with spun hollow fibers of the temperature- and chemical-resistant polymer PBI. Testing was performed with two modules, one with first generation (Gen-1) fibers, and one with second generation (Gen-2) fibers. Operation was at a 50-kWth scale using syngas and syngas supplemented with hydrogen and CO<sub>2</sub>. Results are provided below.

- The hydrogen/CO<sub>2</sub> selectivity in the Gen-2 module increased with increasing temperature. This behavior is a unique property of the PBI hollow fiber membranes; conventional polymer membranes show the opposite effect.
- The 1-inch Gen-1 data showed that operating temperatures above 190°C (374°F) would be required to achieve a hydrogen/CO<sub>2</sub> selectivity of 25. In comparison, the Gen-2 module achieved a selectivity of 25 at temperatures below 140°C. The NCCC field test conditions confirmed that the Gen-2 fibers are superior.
- SRI expects much improved performance for the membranes potted with both bore-side ends open to allow a bore-side flow-through configuration enabling the use of permeate sweep gas to further optimize hydrogen recovery and CO<sub>2</sub> capture.
- Testing confirmed that greater than 90% recovery of CO<sub>2</sub> is possible at operating temperatures above 375°F (190°C).

### ***MTR Proteus Hydrogen Membranes***

MTR continued evaluation of Proteus hydrogen membranes, conducting long-term testing with a four-inch module.

- For the duration of testing on the 50 lb/hr unit, the temperature of the syngas entering the module vessel was maintained at 110°C (230°F), and the syngas feed pressure was kept constant at 170 psig. The syngas feed was not enriched with hydrogen during G-5 testing.
- The module showed hydrogen enrichment (defined as the permeate hydrogen concentration divided by the feed hydrogen concentration) of about 5 for both the G-5 run and for the previous run. The consistent hydrogen enrichment value attests to the high quality of the module and absence of deterioration over the two runs.
- The membrane module performance showed no deterioration over two gasification runs, indicating high quality of the module.
- Between 340 hours and the end of the run, the permeate hydrogen concentration dropped considerably while the feed hydrogen content was virtually unchanged. The drop in permeate hydrogen concentration was due to an increase in the permeate pressure, which lowered the hydrogen partial pressure driving force across the membrane by 85%. The permeate pressure increase was thought to be caused by the accumulation of debris in the permeate piping.

### ***MPT Palladium-Based Hydrogen Membranes***

MPT conducted the first test of a stand-alone, multi-tube palladium membrane for hydrogen separation. Highlights of the testing are listed below.

- The test objectives were to evaluate the physical integrity of the palladium membrane bundle, determine the impact of syngas contaminants in the presence of tar-like species, and assess the membrane's ability to be regenerated. To achieve these objectives, MPT used as the feed gas syngas that was pre-treated with water-gas shifting and desulfurization, but not treated to remove tars.
- Prior to operation, modifications were made to the system to allow in-situ oxidation and regeneration of the membranes, which comprised brief exposure to air at 310°C (590°F).
- During G-5 hydrogen permeance values were lower than expected due to the effects of tar. However, MPT demonstrated that the permeance could be restored in the lab with air treatment at raised temperatures.
- The G-5 testing included 156 hours of syngas permeation run time and 176 hours of membrane regeneration. Three membrane bundles were tested, each consisting of 12 tubes, which were 12 inches in length.
- Though in-situ regeneration was attempted for restoration of membrane activity, the presence of tar in the syngas and residual tar in the system prevented measurements of true hydrogen permeance. However, MPT demonstrated that the permeance could be restored in the lab with air treatment at raised temperatures. The regenerated membranes maintained their original permeance for an extended period in the lab.

### ***TDA Research CO<sub>2</sub> Sorbent***

After completing several successful campaigns at the NCCC with CO<sub>2</sub> sorbent technology, TDA scaled up testing of the CO<sub>2</sub> sorbent process to a small pilot-scale unit tested in G-5. Highlights of the testing are listed below.

- The robust control system allowed for wide range of testing, which permitted fine tuning of the performance for each of the cycle sequences.
- Except for the first few days of testing, the CO<sub>2</sub> removal efficiency exceeded 90%. When the total cycle time was reduced to eight minutes, the CO<sub>2</sub> removal efficiency exceeded 99%.
- As the test progressed and the optimum operating conditions were identified, the CO<sub>2</sub> capacity of the sorbent was improved.
- By optimizing the process cycle to allow faster cycling, TDA reduced the bed size by half in the 0.1-MW skid.