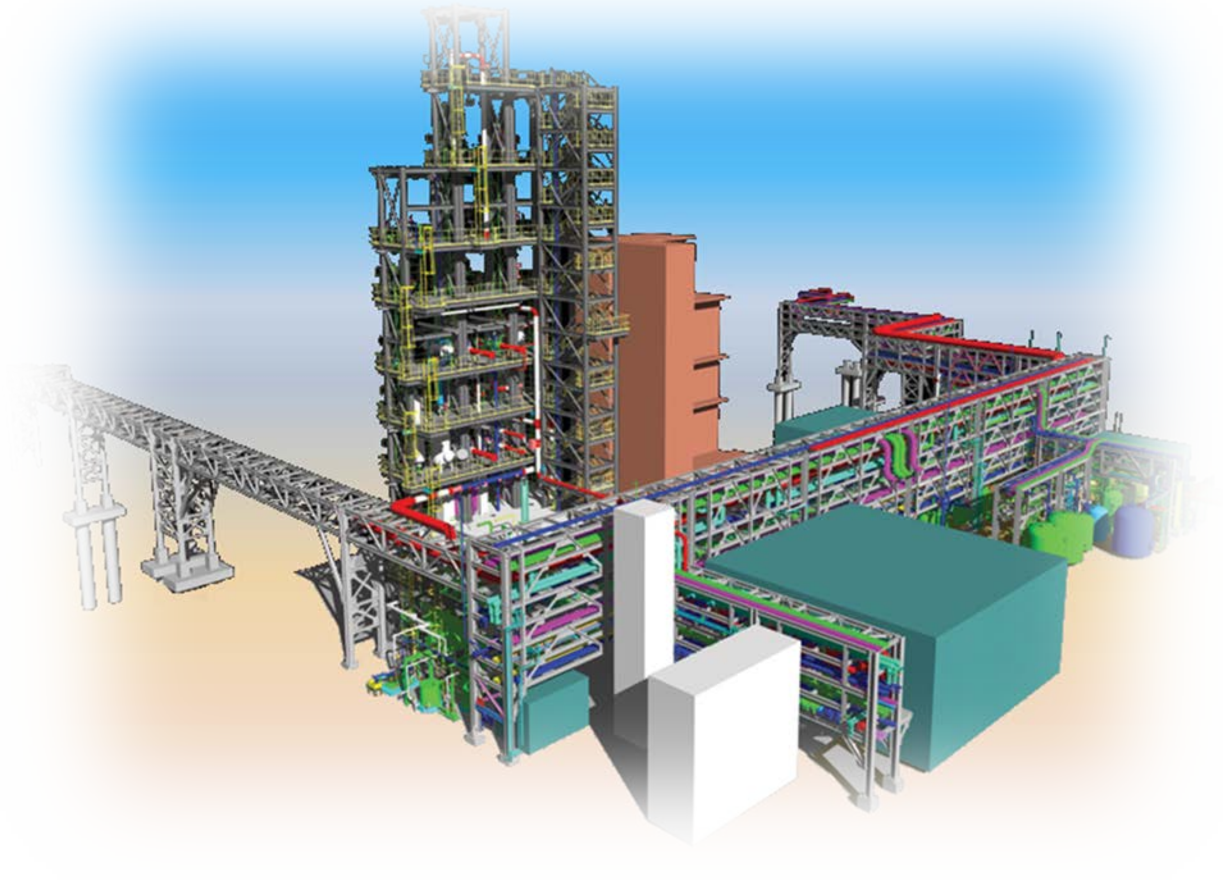
The National Carbon Capture Center
at the Power Systems Development Facility

Topical Report
Budget Period One

Reporting Period: June 6, 2014 – May 31, 2015
Project Period: June 6, 2014 – June 5, 2019



DOE Cooperative Agreement
DE-FE0022596

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Abstract

The Power Systems Development Facility (PSDF) is a state-of-the-art test center sponsored by the U.S. Department of Energy (DOE) and dedicated to the advancement of clean coal technology. In addition to the development of high efficiency coal gasification processes, the PSDF features the National Carbon Capture Center (NCCC) to promote new CO_2 capture technologies for application in existing coal combustion power plants and in the next generation of integrated gasification combined cycle power plants.

The NCCC includes multiple slipstream units that allow technology development of CO_2 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 One reporting period, spanning from June 6, 2014 through May 31, 2015, efforts at the NCCC focused on post-combustion CO_2 capture, gasification, and pre-combustion CO_2 capture technology development. Testing was conducted at the NCCC's Post-Combustion Carbon Capture Center with advanced solvents and solvent systems, a developmental solvent analyzer, sorbent systems, and membrane technologies. The gasification process was also operated to support Fischer-Tropsch, water-gas shift, and COS hydrolysis catalysts, a pressure-swing adsorption process, a mercury sorbent, and gas separation membranes. Preparations for future testing were on-going as well, and involved facility upgrades and collaboration with numerous technology developers.

Acknowledgement

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List of Abbreviations and Acronyms

C2U	Carbon Capture Unit
CCSp	Carbon Capture Scientific
CMS	Carbon Molecular Sieve
COS	Carbonyl Sulfide
DOE	Department of Energy
ELPI+	Electric Low Pressure Impactor
F-T	Fischer-Tropsch
G-1	Gasification Run 1
Gen-2	Generation 2
H_2S	Hydrogen Sulfide
HSX	Hybrid Siloxane
IGCC	Integrated Gasification Combined Cycle
MCC	Motor Control Center
MEA	Monoethanolamine
MPT	Media & Process Technology
MTR	Membrane Technology & Research
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
OSU	Ohio State University
PC	Pulverized Coal
PC4	Post-Combustion Carbon Capture Center
PRB	Powder River Basin
PSA	Pressure-Swing Adsorption
PSDF	Power Systems Development Facility
PSTU	Pilot Solvent Test Unit
SCU	Syngas Conditioning Unit
SRI	Southern Research Institute
SRII	SRI International
SSTU	Slipstream Solvent Test Unit
TPD	Ton per Day
WGS	Water-Gas Shift

1.0 EXECUTIVE SUMMARY

The National Carbon Capture Center (NCCC) at the Power Systems Development Facility (PSDF) 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_2 capture and power generation technologies. The center was established in 2008 to build on the experience, expertise, and infrastructure in place at the PSDF, which has been in operation since 1996.

Project Partnership with DOE

The DOE conceived the PSDF as the premier advanced coal power generation research and development facility of the world, to "serve as the proving ground for many new advanced power systems." Since operations began, the PSDF has been a center for national efforts to develop clean, high efficiency coal-based power generation technologies. After only eight years from the time of construction and commissioning, the PSDF's Transport Gasification process was selected through the DOE Clean Coal Power Initiative for commercial deployment at the new Kemper County Energy Facility.

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. Work at the NCCC supports the development of new power technologies and the continued operation of conventional power plants under CO_2 emission constraints.

In undertaking its mission, the NCCC is involved in a range of activities in the areas of post-combustion CO_2 capture, gasification, and pre-combustion CO_2 capture to develop the most promising technologies for future commercial deployment. The test facilities, shown in Figure 1, include the original PSDF site, which houses the gasification and pre-combustion CO_2 capture processes, and the Post-Combustion Carbon Capture Center (PC4), located at the adjacent Alabama Power E.C. Gaston power plant.

Figure 1. NCCC/PSDF Facilities

Reporting Period

This report covers the work performed during Budget Period One, from June 6, 2014, through May 31, 2015, of the NCCC's second cooperative agreement with DOE, DE-FE0022596.

1.1 Post-Combustion CO_2 Capture Accomplishments

During the reporting period, the PC4 operated in three test runs, supporting 10,000 hours of operation by technology developers. Highlights of the reporting period are listed below.

- Operation of the Pilot Solvent Test Unit (PSTU) with two solvents from Cansolv Technologies with 90 percent CO_2 capture at expected commercial operating conditions
- Characterization of flue gas aerosol and particulate concentration using the Electric Low Pressure Impactor (ELPI+) instrument to assess solvent emissions and control technologies
- Support of DOE's Carbon Capture Simulation Initiative with monoethanol amine (MEA) solvent operation to collect process information that was previously unavailable, including data for dynamic conditions and for wide-ranging steady state conditions
- Testing of a novel solvent analyzer from the University of Edinburgh to support development of real-time instrumentation for future carbon capture plants
- Operation of DOE's Carbon Capture Unit (C2U) in both circulating and batch modes for evaluation of heavy metals accumulation
- Sorbent testing with the SRI International (SRII) sorbent skid to support technology scale-up
- The first simultaneous operation of two pilot-scale technologies: Membrane Technology & Research's (MTR's) 20-TPD scaled-up membrane system and the Linde-BASF solvent process
- Operation of MTR's 1-ton/day (TPD) membrane system for material development and support of the 20-fold scale up
- Initial testing of Ohio State University's (OSU's) bench-scale CO_2 membranes, with testing to be completed
- Testing of the Carbon Capture Scientific (CCSp) bench-scale gas-pressurized stripping process, demonstrating over 95 percent CO_2 capture with over 95 percent CO_2 product purity
- Upgrades to the PC4 to increase capacity and testing flexibility and enhance data quality

1.2 Gasification Technology Accomplishments

The gasification process operated in run G-1 during October and November 2014, with 806 hours of operation achieved. The feedstock used during the run was Powder River Basin (PRB) subbituminous coal, with about 73 hours of the run comprising co-gasification with biomass at 20 wt% of the total feed rate. Less than an hour of interruption of gasification operation occurred throughout the run duration, and over 70 percent of the run consisted of steady-state periods. Steady-state carbon conversion averaged 98.4 percent during coal-only operation and averaged 99.1 percent during biomass co-feeding. The run provided testing opportunity for a variety of developer technologies, as well as continued long-term evaluation of coal feeder instrumentation, gasifier refractory, and hot gas filter elements. Developer technology accomplishments of the G-1 run were:

- The first full syngas operation of the Southern Research Institute (SRI) Fischer-Tropsch (F-T) catalyst system, with effective system modifications based on previous operation at the NCCC, and demonstrating stable operation and catalyst productivity more than four times greater than that of conventional F-T catalysts, with greater than 70 percent selectivity to gasoline- and diesel-range liquid hydrocarbons
- The first operation of a pressure-swing absorption (PSA) process from Air Products, with stable sorbent performance and system operation, good mass balance closures, 99.7 percent removal of hydrogen sulfide (H_2S) and more than 95 percent removal of CO_2 from syngas
- Continued operation of Johnson Matthey's mercury sorbent, demonstrating near complete mercury capture and long-term sorbent stability after more than 4,000 hours of accumulated operation
- Continued operation of a water-gas shift (WGS) catalyst, demonstrating catalyst stability over long-term testing
- Testing of a carbonyl sulfide (COS) hydrolysis catalyst developed for high temperature operation, which showed an average conversion rate of 39 percent

1.3 Pre-Combustion CO_2 Capture Accomplishments

Pre-combustion CO_2 capture testing during the year included more than 1,300 hours of membrane operation, including:

- Operation of the Media & Process Technology (MPT) Carbon Molecular Sieve (CMS) and combined operation with a palladium-based polishing membrane, demonstrating the ability to produce hydrogen with greater than 99 percent purity, and providing process data for further development of MPT's catalytic membrane reactor
- Testing of MTR's Proteus™ hydrogen membrane module, which enriched hydrogen concentration in the permeate to three to four times the feed concentration
- Operation of MTR's Proteus stamp cells from MTR for continued high-temperature stability evaluations, demonstrating good stability and excellent hydrogen separation performance at temperatures up to 194°C

2.0 POST-COMBUSTION CO_2 CAPTURE

The PC4 utilizes flue gas from Plant Gaston Unit 5, a base-loaded, 880-MW gross supercritical pulverized coal boiler fired with Alabama medium-sulfur bituminous coal. 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 (SSTU) are fully integrated systems for comprehensive solvent characterization at pilot- and bench-scale, respectively. An air dilution system is also available for CO_2 capture testing under simulated natural gas flue gas conditions.

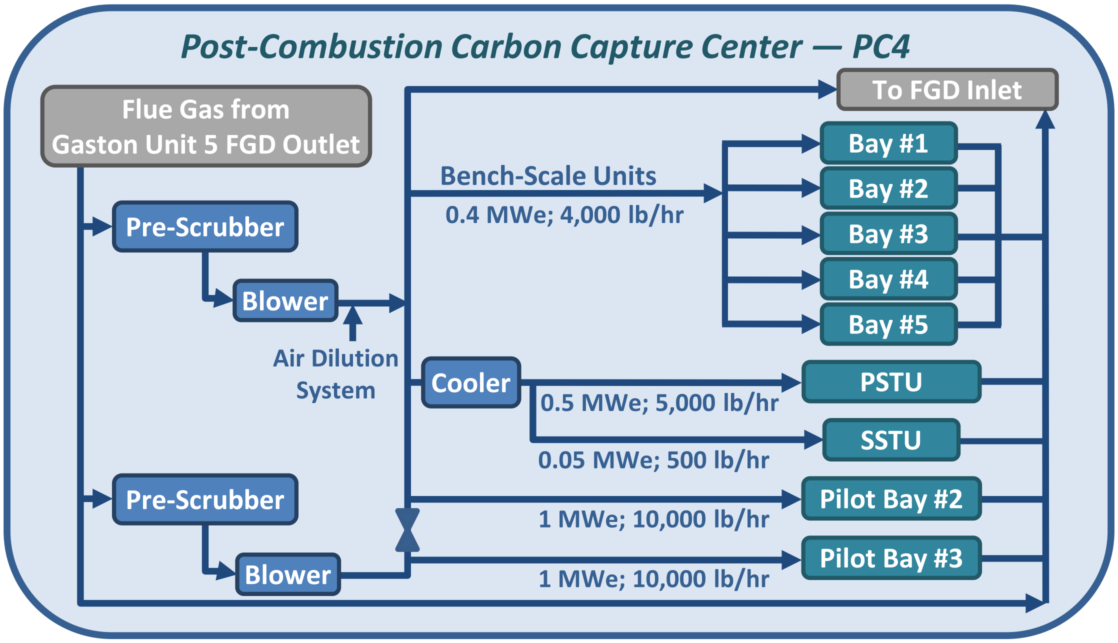

Figure 2. Schematic of PC4 Test Facilities

Figure 3 provides a schematic of the PSTU, which consists of five major sub-systems:

- A pre-scrubber which removes the small amount of SO_2 remaining in the flue gas
- A cooler/condenser unit that cools the flue gas to appropriate reaction temperatures and removes flue gas moisture
- An absorber to promote efficient gas-liquid contacting to remove CO_2 from the flue gas
- A wash tower that cools the CO_2-depleted flue gas, removing trace amounts of entrained solvent
- A regenerator that provides heat to release the CO_2 from the solvent

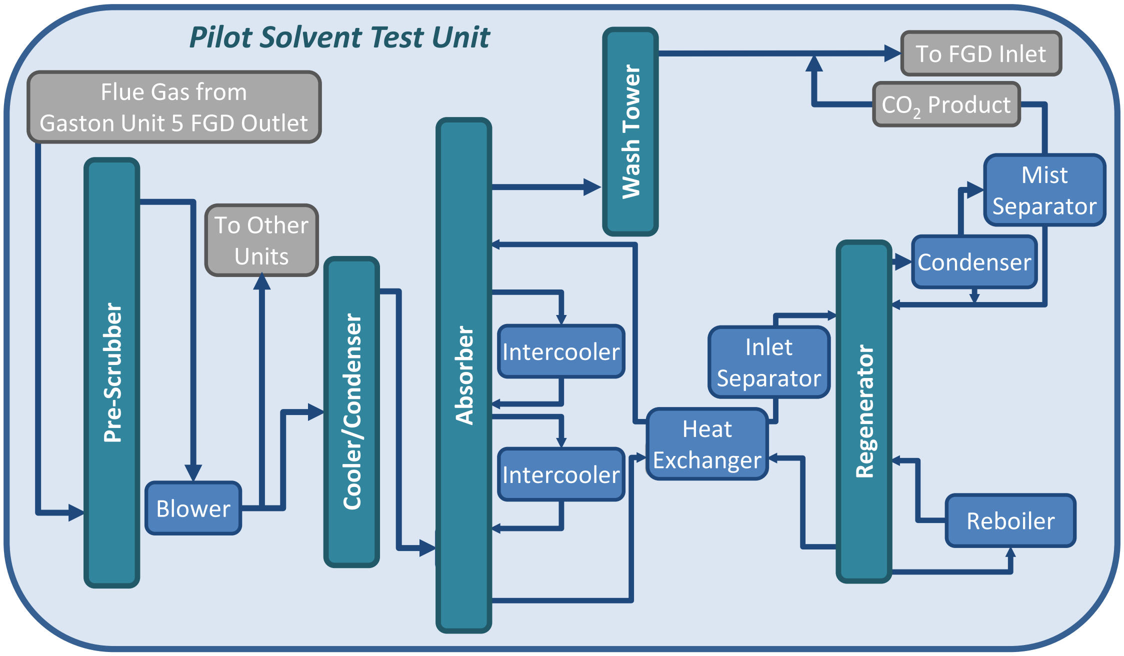

Figure 3. Schematic of PSTU

During the reporting period, the PC4 operated over three runs:

- PO-1, from June through August 2014
- PO-2, from January to March 2015
- PO-3, beginning in May 2015 and continuing through the end of the reporting period and into August 2015

2.1 Cansolv Technologies Solvents

In 2014, Cansolv Technologies conducted solvent testing of two solvents in the PSTU. Beginning in June, a 325-hour campaign was completed with the DC-103 solvent, followed by a 471-hour campaign with the DC-201 solvent lasting through mid-August. These two campaigns extended Cansolv's previous solvent testing with DC-201 under typical coal-fired conditions and under simulated natural gas conditions. The 2014 testing included measurements of solvent emissions with the ELPI+ instrument and operation under hot climate conditions.

2.1.1 Cansolv DC-103 Solvent

During the first portion of the Cansolv DC-103 test campaign, PSTU operating conditions were optimized for the solvent. Table 1 summarizes the optimal process conditions established. After achieving steady state operation at these conditions, the ELPI+ instrument was used to measure the concentration and droplet size distribution of aerosols present in the CO_2 depleted flue gas leaving the wash tower. Samples were taken before and after the installation of a new high efficiency demister in the wash tower to assess the effect on solvent emissions.

Table 1. Optimized Parameters for Cansolv DC-103 Solvent Testing

Test Parameter	Value
Number of Absorber Packing Sections	3
Bottom Intercooler	On
Top Intercooler	Off
Flue Gas Flow Rate	5,000 lb/hr
Flue Gas Temperature	46°C
Flue Gas CO_2 Concentration (Normal Plant Load)	10.8 vol%, dry
Flue Gas CO_2 Concentration (High Plant Load)	11.8 vol%, dry
Lean Amine Circulation Rate	10,400 lb/hr
Lean Amine Temperature	45.6°C
Intercooler Outlet Amine Temperature	33°C
Water Wash Circulation Rate	10,000 lb/hr
Water Wash Liquid Temperature	43°C
Steam Flow Rate (from flow meter)	930 lb/hr
Rich Amine Temperature to Regenerator	114°C
Rich Amine Pressure to Regenerator	50 psig
Regenerator Pressure	14.5 psig

Figure 4 and Figure 5 plot the CO_2 removal and stripping factor calculated for the absorber side and stripper side, respectively. Optimal steady state operation was achieved at around 50 hours of operation. At this point, the configuration with one intercooler in the bottom section of the absorber (the packing sections) was optimized for energy consumption. The average values for the absorber side CO_2 removal were about 4.7 percent higher, and for the absorber side stripping factor, about 4.7 percent lower than for the stripper side.

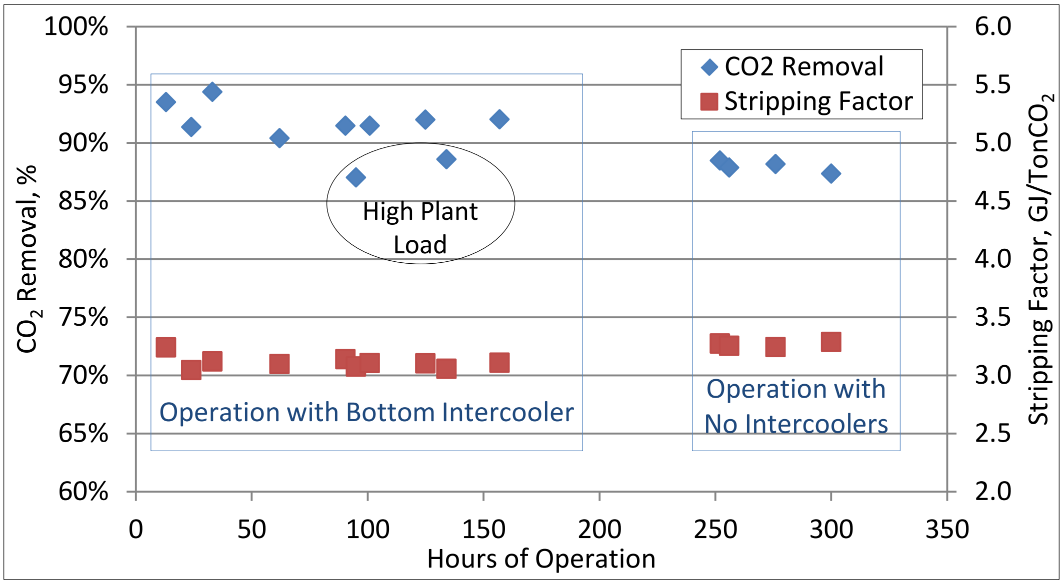

Figure 4. Absorber Side CO_2 Removal and Stripping Factor for DC-103 Solvent

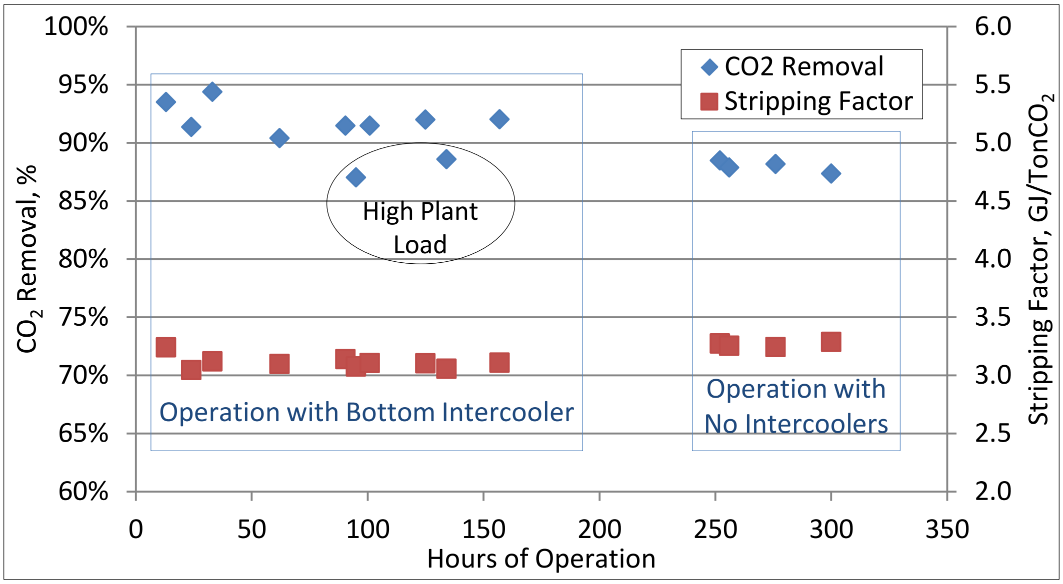

Figure 5. Stripper Side CO_2 Removal and Stripping Factor for DC-103 Solvent

Figure 4 and Figure 5 demonstrate the impact of power plant load on CO_2 removal efficiency. As the power plant load increased, and thus the inlet CO_2 concentration increased (from 10.8 to 11.8 vol% CO_2 dry), the CO_2 removal rate decreased by about 5 percent. However, since the total amount of CO_2 captured remained constant, the stripping factor was also unchanged. This reduction of CO_2 removal rate at higher inlet CO_2 concentration indicated that the liquid flow rate was at near maximum loading.

Also shown in the figures is the impact of operating the bottom intercooler on overall process performance. For normal plant load operations, when the bottom intercooler was removed from service, the CO_2 removal rate decreased by approximately 5 percent, and the stripping factor increased by the same percentage. One test with no intercoolers was performed with the lean amine temperature increased from 45^oC to 60^oC, and the results demonstrated no significant difference in CO_2 removal rate or stripping factor.

2.1.2 Aerosol and Particulate Measurements with ELPI+ Instrument

The ELPI+ measurements provided results for aerosol and particulate matter concentrations and size distributions at three locations:

- Inlet flue gas to the absorber
- Outlet flue gas from the water wash downstream of the original demister
- Outlet flue gas from the water wash downstream of the high efficiency demister

The measurements were taken to characterize the properties of the flue gas used at the PC4, that is, flue gas from a typical coal fired power plant with a wet stack arrangement. In the wet stack arrangement, the flue gas is cooled directly with water from the pre-scrubber upstream of the

CO_2 absorber. The measurements were also used to assess the flue gas after contact with the DC-103 solvent. This was done with the two different demisters to evaluate the impact of standard and high efficiency demisters on percent droplet capture and amine emissions.

Figure 6 provides the ELPI+ measurements of aerosol and particulate concentration and size distributions for the flue gas used at the PC4. The results showed no significant difference in aerosol or particulate concentration or sizes for the three different process locations sampled. The total number of particles was on the order of 10 to 20 million per cubic centimeter, with the majority between 0.1 and 0.3 microns. There was no significant difference in the results with the original, standard demister and the high efficiency demister. Due to the small particle size, neither type of demister would be expected to have significant aerosol or particulate capture.

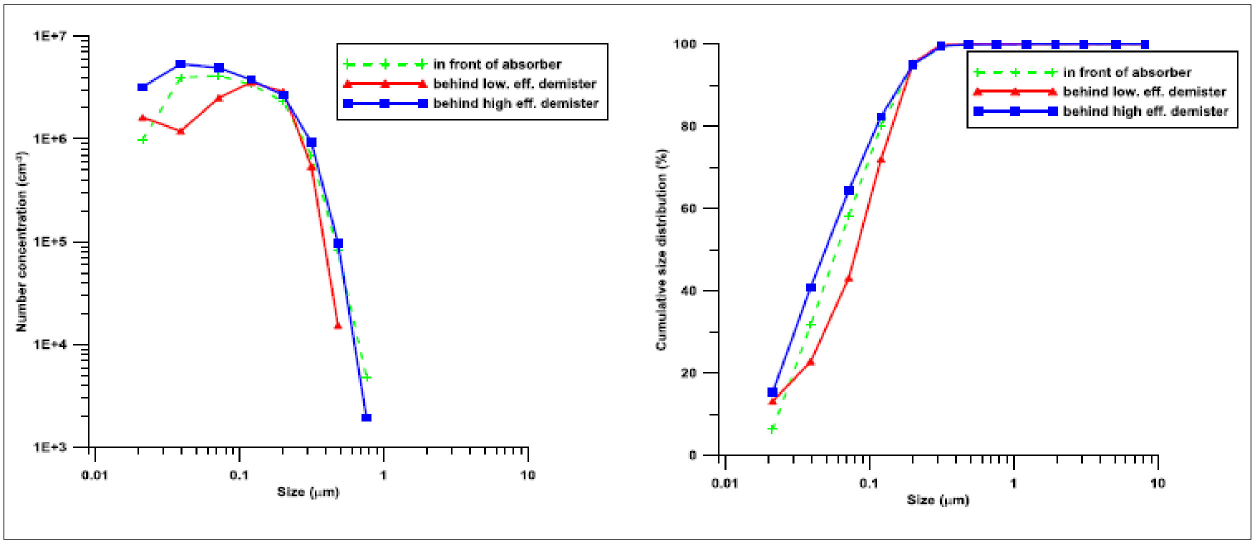

Figure 6. ELPI+ Measurements of Aerosol and Particulate Concentrations during DC-103 Campaign

Laborelec has taken ELPI+ measurements at different coal fired power plants throughout Europe, with results showing that the majority of aerosols and particulate were smaller than 0.3 microns. While operating with the DC-103 solvent, there was no change in particle size at the outlet of the absorber because of the solvent's low volatility. However, with a higher volatility solvent such as MEA, the measured size at the absorber outlet would be significantly larger.

2.1.3 Cansolv DC-201 Solvent

The DC-201 test required operation under diluted flue gas conditions to simulate the flue gas from a natural gas fired power plant, to mimic the expected near-term commercial application. To evaluate the effects of solvent degradation products, the testing utilized solvent that had operated in previous testing in the PSTU.

A major test objective was to operate under hot climate conditions at 90 percent CO_2 capture to assess energy consumption and degradation rates. Under the hot climate conditions, the flue gas temperature was 45 to 50°C and the lean solvent temperature was 54°C, compared to 35 to 40°C flue gas temperatures and 40°C lean solvent temperature under previous, cooler conditions. Figure 7 plots the stripping factor versus liquid-to-gas ratio for the two climate conditions. The optimized energy consumption under hot climate conditions was about 6 percent higher than under the cooler conditions. This was expected since the equilibrium rich CO_2 loading is lower at higher absorber temperature, and hence a higher circulation rate and steam rate is required per unit mass of CO_2 captured.

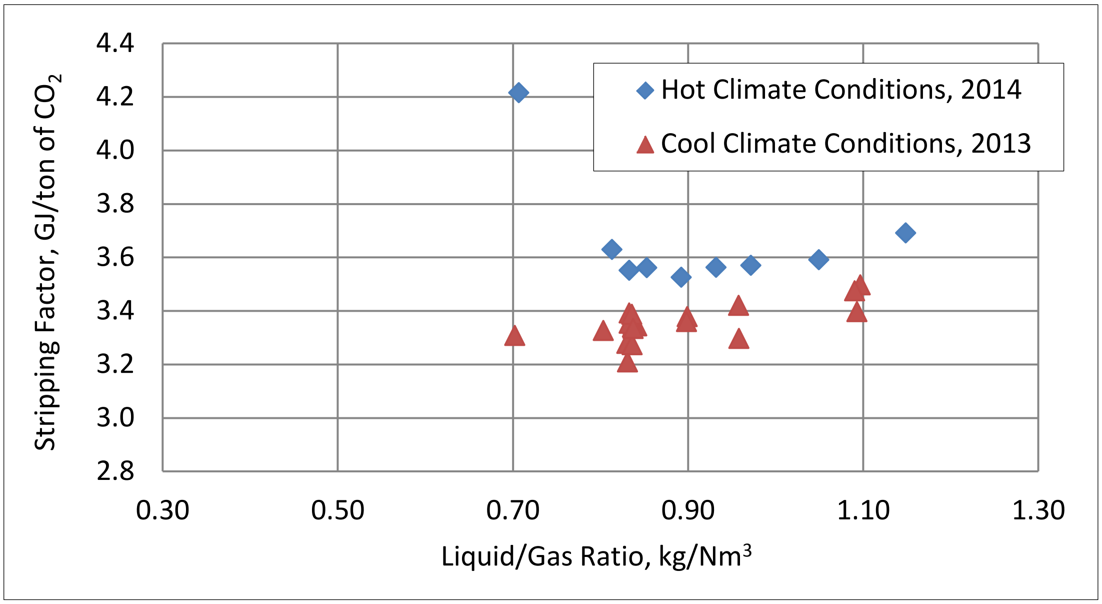

Figure 7. Comparison of Energy Consumption for Mild and Hot Climate Conditions

With the relatively short test duration, a clear trend of degradation rate was not apparent. Although a strontium tracer was added to the solvent to identify any physical entrainment of non-volatile species in the exiting flue gas, it proved ineffective due to solubility problems.

Another test objective was to measure amine emissions from a fresh amine solution. Table 2 gives the results of these measurements. As expected, the contaminants present in the flue gas from the coal-fired plant caused higher emissions. The fresh solvent solution emitted less than used solvent solutions in which degradation product had accumulated.

Table 2. Amine Emissions with Used and Fresh DC-201 Solvent

Gas Type	*Solvent Condition*	*Amine Emission Ratio to Air*
Air	Used	1.0
Coal Condition	Used	26.2
Air	Fresh	0.16

2.2 MEA Solvent for DOE Carbon Capture Simulation Initiative

MEA testing was performed in the PSTU to support DOE's Carbon Capture Simulation Initiative. The testing occurred over two periods in June and August 2014, with the data generated to be used to validate models of comparable carbon capture systems. Dynamic and parametric testing was included as part of the model validation. Dynamic testing focused on modeling the system response to operator or plant changes, and parametric testing validated the model output for steady state periods.

The dynamic testing included varying of flue gas, solvent, and steam flow rates. While the system was in steady state, one of these adjustable parameters was increased and then decreased in a step-wise pattern, and samples of both rich and lean solvent were collected every five to fifteen minutes, depending on the parameter. The objective was to introduce the next change before the system could equilibrate from the previous change. Following the dynamic testing, parametric testing was completed, and mainly comprised of conditions utilizing only one absorber bed. Data were taken from 17 steady-state periods for comparison with the predicted results from process simulation software for two cases involving the absorber and regenerator. A total of 408 hours on flue gas were accumulated for these tests.

Preliminary comparisons of the steady-state data to DOE's deterministic model predictions were made separately for the absorber model and the regenerator model. A total of seventeen cases were simulated, and a sample of six of these is presented. For the absorber model, the major input of interest was the liquid-to-gas mass ratio. For the regenerator model, the major inputs of interest were the rich solvent flow and the reboiler duty. These inputs are given in Table 3.

Table 3. Inputs for Steady-State Absorber and Regenerator Simulations with MEA

Case	*L/G Mass Ratio*	*Rich Solvent Flow (kg/hr)*	*Reboiler Duty (kW)*
K1	3.00	7242	434
K3	1.41	3335	431
K4	1.41	3343	431
K9	1.41	3337	167
K11	3.02	7241	429
K16	1.41	4347	423

Comparisons of model predictions and NCCC operational data for the absorber are plotted in Figure 8. The model predictions matched the percent CO_2 capture operational data well when the CO_2 capture rate was high. The model generally under-predicted the temperature of the rich solvent stream in the absorber outlet. This discrepancy may be due to the model's inaccurate characterization of the heat of absorption of the MEA-H_2O-CO_2 system. Work is ongoing to further develop the model's accuracy in this area.

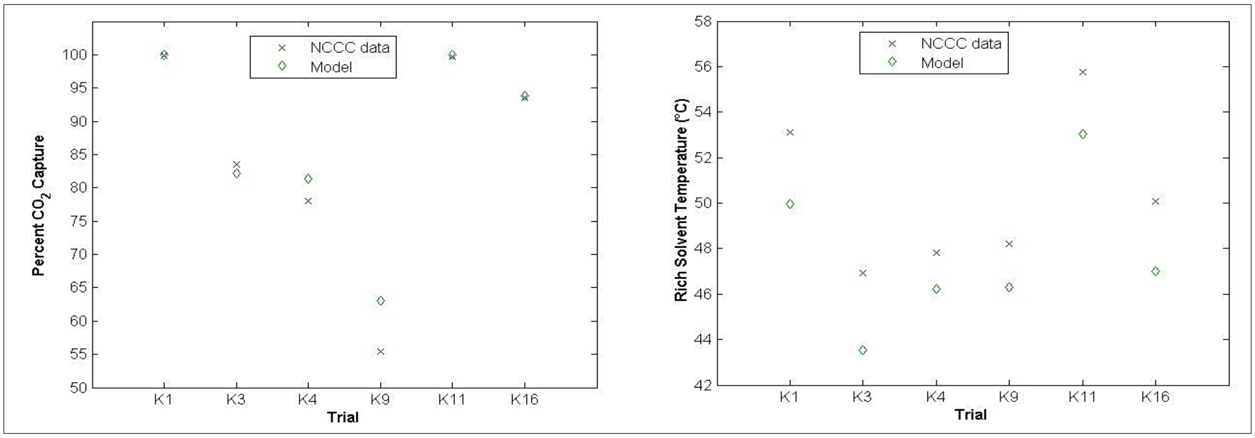

Figure 8. Comparison of Model and NCCC Data for Absorber Operation with MEA

For the stripper model, the output variables of interest are the CO_2 loading and temperature of the outlet lean solvent. The comparisons are given in Figure 9. The model generally over-predicted both the loading and temperature of the lean solvent stream. These discrepancies may be reconciled with future modeling of the thermodynamics of the system and uncertainty quantification of the property models, hydraulic models, and mass transfer models.

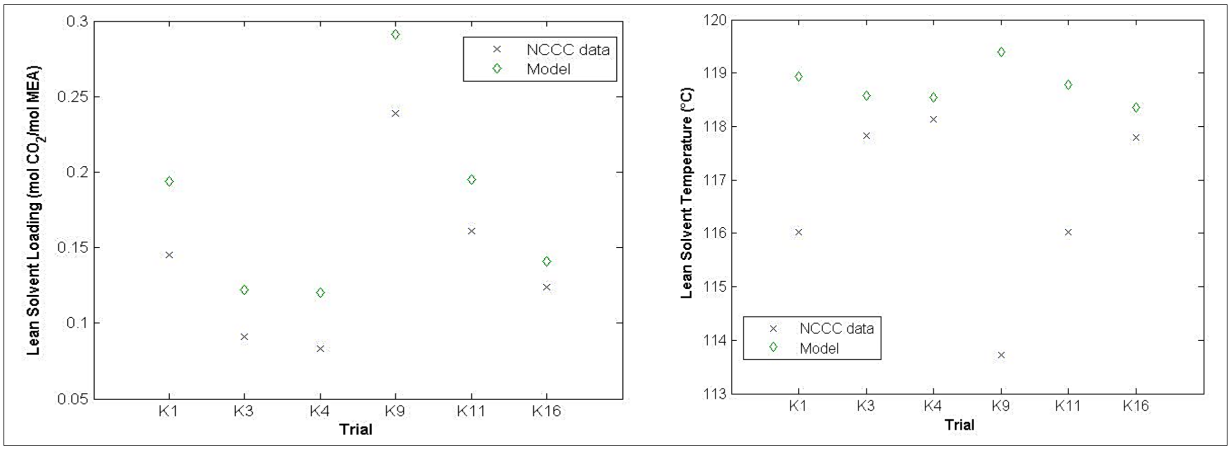

Figure 9. Comparison of Model and NCCC Data for Regenerator Operation with MEA

2.3 University of Edinburgh Solvent Analyzer

During the MEA testing performed for the DOE's Carbon Capture Simulation Initiative, the University of Edinburgh tested a real-time solvent analysis device. The device is being developed as a low-cost solvent analysis technique capable of determining solvent concentration and loading within a ten-second response window. This near real-time response is a significant improvement over current state-of-the-art technologies for solvent analysis that can take up to 30 minutes to provide data. The University of Edinburgh device would allow for changes in process variables such as load demand in a commercial carbon capture process. The test apparatus uses Inferential Solvent Analysis to measure solvent concentration and loading online. The advantages of the device over commercially available systems include:

- Simple on- or off-line calibration, resilience to solvent complexities
- Significantly smaller capital costs and maintenance costs
- Compatible with automated control systems and data logging

Figure 10 plots the continuous measurements of CO_2 loading and amine concentration taken by the analyzer. Points on the graph correspond to discrete samples taken and analyzed in the lab using standard industry methods, and the statistical error ranges for the analysis performed are provided for each sample point.

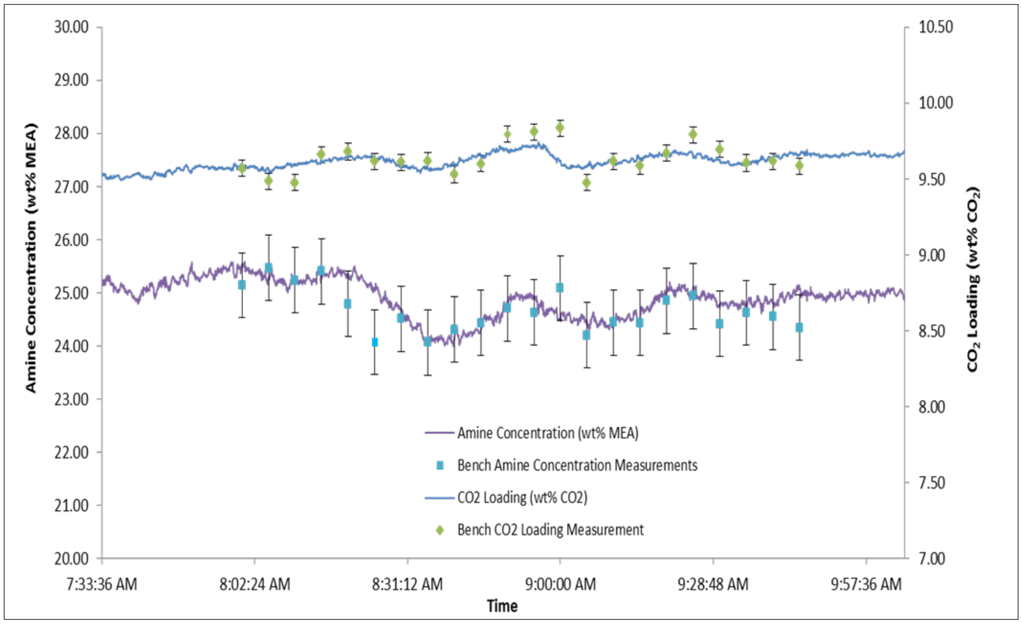

Figure 10. Preliminary Results of the University of Edinburgh Solvent Analyzer

2.4 DOE C2U Sorbent Unit

DOE designed the C2U to test the CO_2 removal with sorbents composed of amines on a solid substrate. The unit, which utilizes fluidized beds for both absorption and regeneration, was designed and constructed at the National Energy Technology Laboratory. NETL operated the unit for about three years in both circulating and batch modes under a variety of conditions, using two sorbents composed of polyethylenimine on a silica substrate. Testing of the C2U was conducted at the PC4 in 2014. The focus of these tests was to evaluate the accumulation of heavy metals such as selenium on the sorbent. Testing was conducted in circulating and batch modes of operation. Figure 11 shows the C2U as it was installed at the PC4.

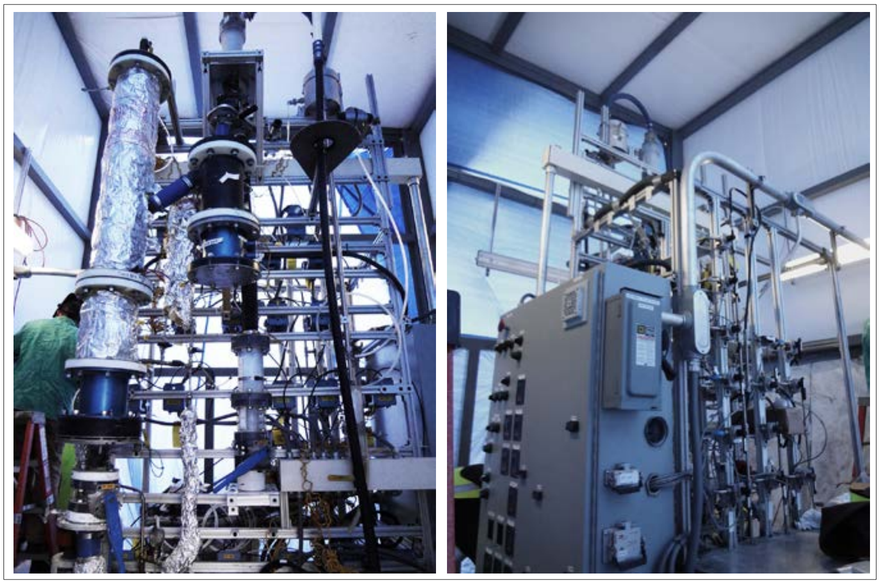

Figure 11. Assembly of the DOE Sorbent Unit

Results of Circulating Tests

Data was acquired for approximately six-hours per day during circulating tests. Initially, the sorbent adsorbed most of the CO_2. However, as hours of operation progressed, the adsorption rate declined dramatically. Although detailed analysis of the degradation in performance of the system was not performed, incomplete regeneration of the sorbent was thought to be the cause of the reduced performance, resulting in an elevated lean CO_2 loading and a concomitant lower working capacity.

Post-test thermo-gravimetric analysis of sorbent samples from the circulation tests showed no permanent loss of CO_2 capture capacity. Complete regeneration of the sorbent would allow the system to attain the performance initially observed during the first few hours of testing with a fresh inventory of sorbent.

Results of Batch Tests

After the circulating tests were completed, the C2U was reconfigured to perform a continuous batch test, and 2.4 kg of new sorbent was added to the regenerator. The goal of this test was to supply flue gas to a single bed of sorbent for an extended period of time (1,000 hours) and subsequently analyze the sorbent composition. The only instrumentation in use was a vacuum pump, a rotameter, and a magnehelic pressure gauge across the bed.

The slipstream did not have sufficient pressure to operate within the test unit, thus the pressure was boosted using vacuum pumps. Two vacuum pumps were used in parallel to deliver a flow rate of approximately 30 slpm of flue gas through the system.

The flue gas initially supplied to the unit for the batch tests was diluted with air to simulate natural gas combustion products to accommodate other PC4 users. Although the sorbent was exposed to the diluted flue gas for 346 hours, the equivalent amount of flue gas exposure was

115 hours due to dilution. After transitioning to regular coal-fired flue gas composition, an additional 282 hours of testing were completed before a planned plant outage, for a total equivalent flue gas exposure of 397 hours. The end result was that 2.4 kg of sorbent was exposed to the equivalent 357,000 standard liters (12,600 scf) of coal-fired flue gas.

Post-test thermo-gravimetric analysis of sorbent samples from the batch tests showed no permanent loss of CO_2 capture capacity. Samples of the sorbent from the batch tests were also analyzed for trace elements. The amount of arsenic, chromium, lead, mercury, and selenium for these samples was compared to the amount required to be considered a hazardous waste by the EPA. In all cases, the trace element concentrations were significantly lower than the hazardous waste standards.

Table 4 provides the trace element analysis results for sorbent samples taken following each test period—circulation testing and batch testing with the two types of flue gas. While the amount of selenium for all the samples was below the detection limit of 1 ppm, the amount in the flue gas was estimated to be about 23 ppm. Because the semi-volatile metals like selenium likely drop out of the flue gas by partitioning (for example, in the fly ash collection device and in the flue gas desulfurization scrubber), flue gas sampling directly upstream of the sorbent skid would be helpful in future testing to assess the amount of metals reaching the sorbent.

Table 4. Analysis of C2U Sorbent Samples

	Circulation Tests	*Batch Tests with Diluted Flue Gas*	*Batch Tests with Typical Flue Gas*
Sample Date	6/15	8/15	8/25
Equivalent Exposure Hours	44	115	397
Arsenic, ppm	0.22	0.25	0.22
Chromium, ppm	<5	<5	<5
Lead, ppm	0.35	0.45	0.77
Mercury, ppm	0.003	0.005	0.005
Selenium, ppm	<1	<1	<1

2.5 SRI International Sorbent

SRI International, through work funded by the DOE, is developing a novel carbon sorbent process for CO_2 capture. The SRII sorbent process includes a contactor device of structured packing which distributes the free flowing particles and provides high contact efficiency with the gas stream at a low pressure drop. The vertical design allows the adsorber and regenerator to be incorporated in a single vertical column. The sorbent features several advantages, including:

- Particles that are about 1 mm, free flowing, and resistant to attrition
- Low cost with a high CO_2 loading of 0.1 to 0.2 kg/kg in the range of 20 to 100^{o}C

- Low heat of reaction, in the range of 25 to 28 kJ/mole of CO_2, and CO_2 is released at atmospheric pressure at temperatures in the range of 80 to 100^oC

SRII's 40-kWe bench-scale unit is designed to process about 70 cfm (250 tons) of CO_2 annually and operates at near ambient temperature using a falling microbead reactor in which the sorbent granules (microbeads) fall down by gravity counter-current to the flue gas flow. The adsorbed CO_2 is removed by heating the CO_2-loaded sorbent to 100°C in contact with low-pressure steam. The regenerated sorbent is dehydrated of adsorbed moisture, cooled, and lifted back to the adsorber. The process is designed to produce nearly pure CO_2 from the stripper. The design was tested in a smaller unit at a 3.5 kWe-scale in a small boiler at the University of Toledo for 130 hours, demonstrating CO_2 capture efficiency of 99 percent and producing over 98 percent pure CO_2. Operational data from the NCCC testing will be used for further scale-up of the process to a 1-MWe pilot plant unit.

The 40-kWe test skid was commissioned in the fourth quarter of 2013. SRII continued to operate the test skid in 2014 with flue gas to obtain additional data and experience. Following the replacement of a heat exchanger for the dehydrator, SRII performed additional testing of its sorbent process for two weeks with coal-derived flue gas, achieving greater than 90 percent purity in the stripped CO_2 stream with steam regeneration, and final testing was conducted in August. The operation of the unit indicated certain modifications were necessary for consistent and reliable operation. The test results are summarized below:

- Continuous operation was achieved by using a combination of indirect and direct steam heating of the sorbent in the CO_2 stripper. The indirect heating demonstrated the possibility of heat recovery from the hot dehydrator exhaust.
- A steady flow of 1,200 liters/min flue gas was achieved. The flow was somewhat less than the design flow of 1,800 liters/min. While the target CO_2 capture efficiency was 90 percent, the test results showed that only 70 percent capture was achieved. The lower capture rate was attributed to less than optimal adsorber height.
- The concentration of CO_2 in the stripper outlet was 93 percent. Based on SRII's previous experience, the purity increases with steady state run time when gas flows are optimized.

Operational issues encountered were mostly mechanical and were not uncommon for technology scale-up progression. More conservative designs could have been adapted, but the design parameters were pushed to better expose the operational limitations. Lessons learned that will be applied to the pilot design are listed below:

- The pneumatic lift of the sorbent microbeads is not the preferred design for the pilot-scale unit. A bucket elevator will be used to lift the sorbent microbeads.
- Pinch valves were used successfully to control the flow of the sorbent microbeads within the integrated column.
- Heat exchanger tube density should be increased to allow for more efficient heating and cooling of sorbent.

- Direct steam injection should be minimized by preheating the sorbent microbeads.
- Structured packing effectively separates sorbent beads with very low pressure drop. Separators made of this packing can be operated hot and do not become plugged by accumulation of fines, but require multiple layers of packing for complete separation. Filters may be needed to capture any fines generated during operation.
- Baseline heat loss with no sorbent or supplied flue gas was 60 percent of total heat applied through steam addition, indicating the non-adiabatic nature of small bench-scale units. The heating of the sorbent without CO_2 capture and release accounted for another 25 percent of the steam used. Only the remaining 15 percent of heat energy applied was used to strip the CO_2 from the sorbent. A large system will use heat more efficiently, reducing the steam demand per unit of CO_2 captured.

2.6 MTR 1-Ton/Day CO_2 Membrane System

Beginning in 2011, MTR has been testing polymeric Polaris™ membranes for separating CO_2 from coal-derived flue gas at the PC4. The 1-TPD membrane system includes two membrane module designs required for commercial units, cross-flow membrane and countercurrent-swept membrane modules. Operation of the 1-TPD system during the reporting period occurred during runs PO-1 (July through August 2014) and PO-2 (January through March 2015). Parametric tests were performed on individual cross-flow membrane modules having different designs. Four modules installed in two different vessels were tested. Table 5 provides a description of the modules and the test history.

Table 5. Cross-Flow Modules Tested on the MTR 1-TPD System in August 2014

Module Number	*Membrane Description*	*Testing Period*
6706	Base-Case	I: 12/2012 to 07/2013; II: Since 01/2014
7143	Low-Cost	I: 07/2013 to 10/2013; II: Since 01/2014
7592	Low-Cost (different support layer)	I: Since 01/2014
7595	Low-Cost (different support layer)	I: Since 01/2014

Figure 12 shows the CO_2 concentration in permeate streams for the individual modules tested with regular flue gas feed in August. Modules 7592 and 7595 were tested for the first 90 hours, followed by the testing of modules 6706 and 7143. Comparable CO_2 enrichment rates were achieved with the two groups of modules. However, more CO_2 was removed from the flue gas when the system ran with modules 6706 and 7143 for the cross-flow stage, indicating CO_2 permeance values of these modules were higher than for modules 7592 and 7595.

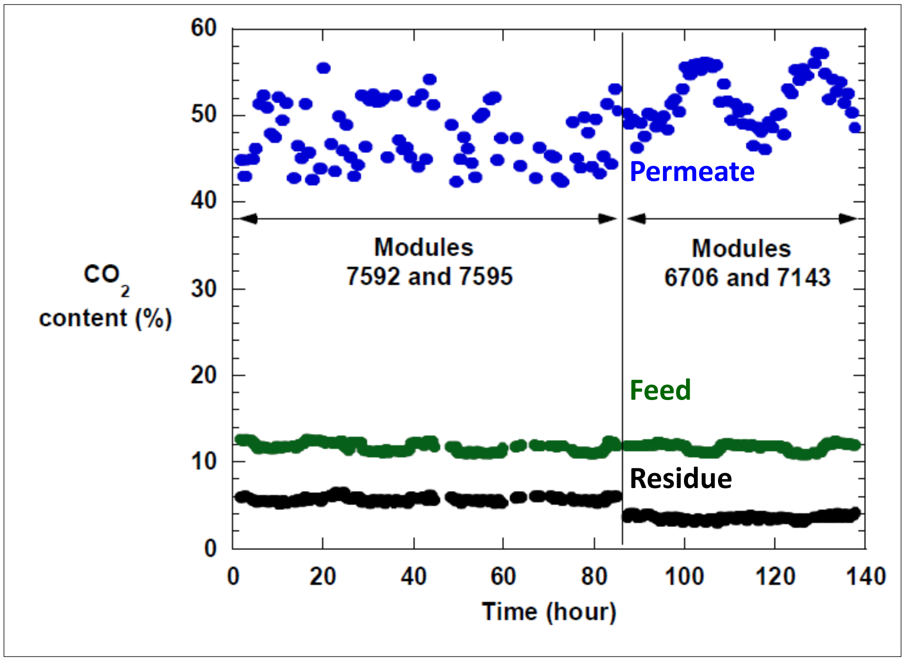

Figure 12. CO$_2$ Content of Inlet and Outlet Gas Streams of the MTR 1-TPD Membrane System during Operation in August 2014

MTR replaced the membrane modules with new ones to continue material evaluations, and operation resumed in 2015. Figure 13 provides an excerpt of the performance during early 2015.

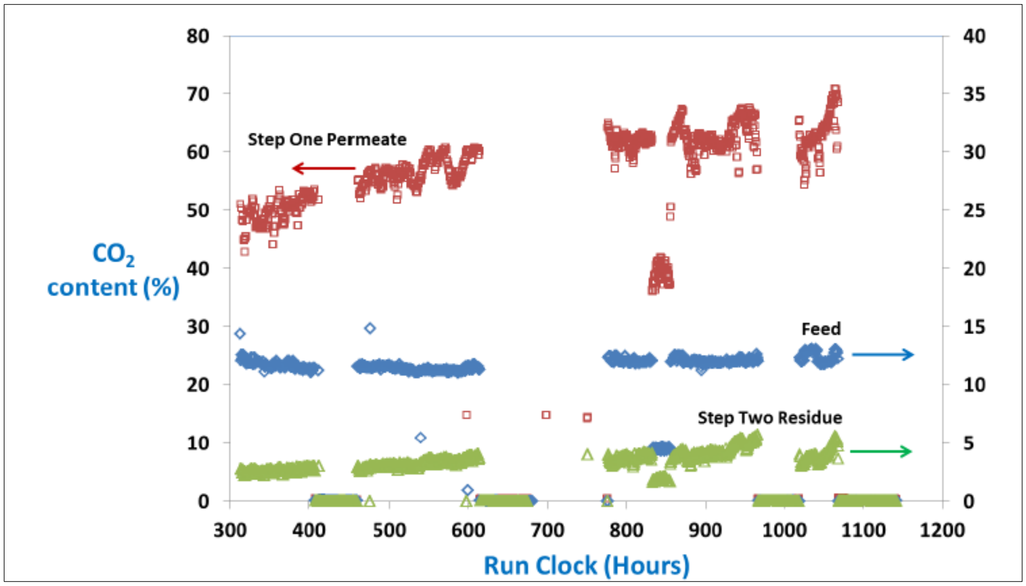

Figure 13. CO$_2$ Content of Feed and Permeate streams for the 1-TPD Membrane System in Early 2015

The membrane enriched CO$_2$ from a feed concentration of about 12 percent to between 50 and 70 percent in the permeate, representing an enrichment factor of 4 to 6. The system generated a treated flue gas between 3 to 5 percent CO_2 as the second step residue stream. The performance was defined by the external winter weather with feed streams cooling from around 25°C at the start to 13°C. Lower feed temperature results in lower permeate flux in both stages, lower stage cut in step one, higher CO_2 concentration in the first step permeate and residue and in the second step residue (the treated flue gas). The fairly steady trend to cooler temperature caused a steady shift in observed CO_2 content. These results are consistent with that of previous operating experience.

2.7 MTR 20-Ton/Day CO_2 Membrane System

In 2014, MTR completed installation and commissioning of the scaled-up, 20-ton/day CO_2 membrane system. The system first operated in 2015 during run PO-2, and for PO-3 operation, a high efficiency plate-and-frame membrane module was added to replace the conventional spiral-wound design.

The system was commissioned on flue gas in January 2015. During PO-2, the system ran intermittently on flue gas due to cold weather issues on the NCCC side, miscellaneous system issues on the MTR side, and the installation of the plate-and-frame sweep module skid. In early March, cold weather cooling water supply issues on the NCCC side tripped the 20-TPD system causing damage to a critical flow switch. Due to the lead time of a replacement part and scheduling considerations, the 20-TPD system did not run for the remainder of PO-2. During PO-2, the 20-TPD system operated on flue gas for approximately 325 hours with CO_2 capture rates ranging from 85 to 95 percent.

The main goal of the PO-3 campaign was to operate the plate and frame sweep skid as the second step of the 20-TPD system for a minimum of 500 hours to validate the lab performance values and demonstrate the stability of the new module design under real coal-fired flue gas conditions. Another goal was to determine the various operating parameters of the 20-TPD system under summer conditions (ambient temperatures of 32°C and higher) compared to the sub-freezing winter conditions of PO-2.

The plate and frame sweep skid was on-line as the second stage step of the 20-TPD system for the duration of PO-3. This allowed for direct comparison to the spiral sweep modules used as the second step during PO-2. The field data for the plate and frame modules is consistent with lab data and confirms the significantly lower pressure drop with the new module design. The plate and frame sweep modules have roughly four times lower pressure drop than the spiral wound sweep modules, which, at full scale, amounts to an energy savings of about 10 MWe.

Downtime of the 20-TPD system was minimized during PO-3 due to lessons learned during PO-2. The 20-TPD system with the plate and frame sweep skid consistently captured CO_2 at a rate of around 87 percent, with capture rates over 90 percent under certain operating conditions. The system ran on flue gas for 900 hours, exceeding the original goal of 500 hours and demonstrated the performance of both the 20-TPD system and the plate-and-frame sweep skid.

2.8 Ohio State University Membranes

After fabricating new membranes that showed good performance in lab tests, OSU shipped their membrane equipment to NCCC in May 2015. The skid, which includes an oven unit, a membrane module, and a gas chromatograph (GC), was installed inside the PC4 gas analytical lab, as shown in Figure 14. Testing began on May 27 and will conclude in June.

Figure 14. OSU Membrane Skid Installed in PC4 Gas Analysis Lab

2.9 Linde-BASF Solvent Pilot Plant

Linde and BASF completed installation in 2014 of a 1-MWe CO_2 capture pilot plant, and operation began in January 2015. The technology incorporates BASF's novel amine-based process along with Linde's process and engineering innovations. The group completed parametric tests to achieve target performance and will began long duration tests in late 2015 to demonstrate solvent stability and obtain critical data for scale-up and commercial application. Through June, the Linde-BASF process had operated for close to 2,000 hours.

The pilot plant was typically operated at 10,500 lb/hr (nominal 1-MWe capacity) except for periods when higher flue gas flow was available at up to 15,500 lb/hr (expected capacity). The CO_2 concentration in the flue gas was 11.5 vol% on a dry basis, and the oxygen concentration was about 7.6 vol%. The desorber pressure was typically set at 2 bar. Daily batch analysis for water, amine, and CO_2 loading in rich and lean solvents to adjust water balance were performed using titrations. For confirmation, a significant amount of gas chromatograph analysis was performed by NCCC. The titration analysis was later extended to include condensate from the wash water circulating loops. Solvent samples were also collected and sent to BASF for detailed analysis in their Michigan laboratories.

Results showed that a 90 percent CO_2 capture rate is easily achieved, with the capture rate adjustable by changing the steam flow rate. A CO_2 product purity of 99.9 percent on a dry basis was typically achieved during the tests. Low oxygen impurity levels in the CO_2 product make it suitable for enhanced oil recovery applications. The regenerator steam consumption of more than 2.8 GJ/tonne CO_2 was achieved during a week of parametric testing at a given flue gas rate and variable solvent circulation rate with room for further optimization. The initial operations and testing phase validated the functionality of the following system components: high capacity structured packing in the absorber sections; absorber gravity flow inter-stage cooler; operation of the flue gas blower downstream of the absorber operating at slightly below atmospheric pressure; and unique reboiler design with potential for cost savings at large scale.

The second campaign began in May 2015, and included parametric testing focused on energy optimization including lean-rich solvent heat exchanger optimization, emissions minimization, and demonstration of desorber pressures up to 3 bar. Preparations were underway to perform isokinetic sampling of the treated flue gas to measure aerosols and amine emissions. Long duration tests aimed at solvent stability demonstration will be planned during the third campaign at the end of 2015 and will continue into 2016. Several key challenges and lessons learned during the initial operations included:

- Cold weather conditions, with temperatures dropping below the design temperature of 9^oC for several days, caused freezing of water and solvent lines, which disrupted operations.
- Managing the water balance required adjustment of multiple parameters. For a given flue gas inlet temperature to the absorber and demineralized water addition at the wash section, the temperatures in the wash system and the stripper reflux had to be set by adjusting the cooling water flows to the heat exchangers and the water removal rate from the reflux line.
- Changes in cooling water temperatures during day and night caused significant disturbances to the steady operation of the pilot plant as manual intervention to change the flow rate setting was required at different temperatures.
- The safety requirements for the hydrogen used to measure total hydrocarbon emissions in the treated gas and CO_2 product using flame ionization detection were addressed jointly by Linde and NCCC. A micro-cylinder of hydrogen was procured, and several components in the hydrogen supply line were modified to comply with the area classification requirements for hydrogen use.
- The operational stability of the pilot plant was substantially improved by appropriate setting of water flows in the wash sections and adjustment of the valve in the two phase flow line transferring the rich liquid from the rich-lean heat exchanger to the regenerator.

2.10 Carbon Capture Scientific Gas-Pressurized Stripping Solvent Process

Carbon Capture Scientific’s gas-pressurized stripping solvent process is designed for solvent regeneration at high pressure, thus reducing CO_2 compression requirements. In 2014, the unit was installed in the bench-scale area, as shown in Figure 15, and commissioning was completed. The first flue gas operation occurred in January 2015.

Figure 15. Carbon Capture Scientific Process Installed at the PC4 Bench-Scale Area

During February, CCSp successfully operated the integrated process with solvent. Initially, the system was unable to achieve the targeted 90 percent CO_2 capture rate under nominal design conditions. Based on analysis of solvent component concentrations and water levels, CCSp determined that the solvent was over-diluted from the manufacturer, as the water concentration was 10 percent higher than specified. With the correct solvent concentration, the system achieved the desired performance at design conditions, and parametric testing was completed. The unit demonstrated over 95 percent CO_2 capture with 95 to 96 percent CO_2 product purity. Steady state operation is shown in Figure 16.

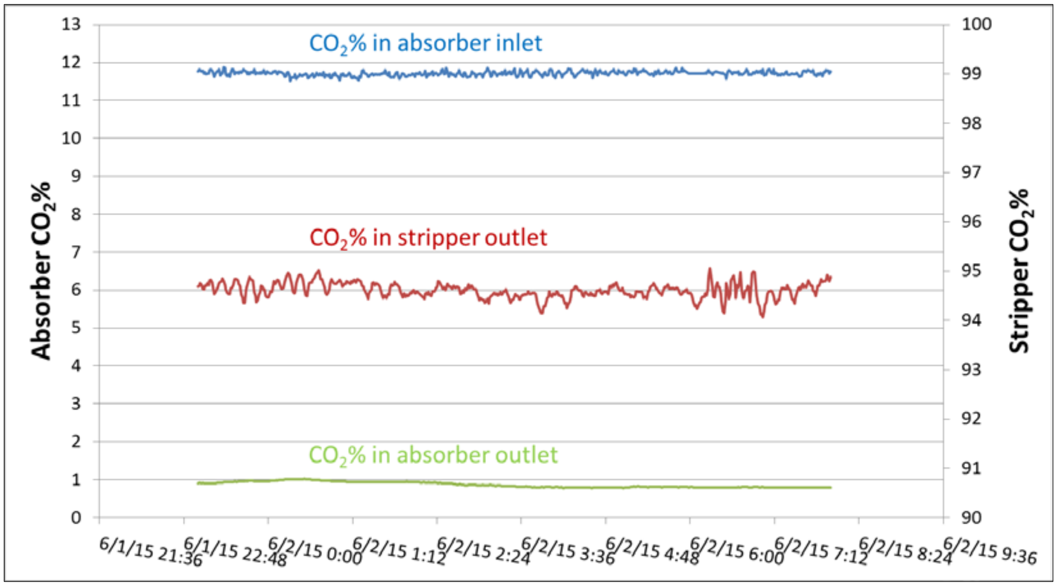

Figure 16. CO_2 Concentrations during Steady Operation of Gas-Pressurized Stripping System

While operating with high ambient temperatures, the skid accumulated water during the day and lost water overnight. The fluctuation of the water concentration in the solvent influenced the performance of the overall process due to the changing amine concentration. To maintain the optimum amine concentration, fresh amine was added periodically. CCSp will complete testing in August 2015.

2.11 PC4 Modifications

Modifications were ongoing to increase the PC4 capacity and flexibility. The most significant of these projects are listed below.

- Final construction was completed for a project to increase the scrubbed flue gas capacity at the pilot-scale test area. The project involved relocation of the original PSTU blower and installation of a new pre-scrubber and associated equipment.
- The NCCC continued progress on the Slipstream Solvent Test Unit to provide a bench-scale system available to technology developers. Design and construction for needed modifications were completed. During commissioning, some additional needed modifications were identified and begun.
- To improve the accuracy of PSTU steam flow rate measurements, modifications were made on the arrangement and piping of the steam flow meters and flow control valves to maintain superheat at the measurement point. A condensate system was also added for measurement verification.
- A fourth floor addition to the PSTU was completed to provide space for technology developer equipment.

3.0 GASIFICATION

The NCCC gasification process, represented in Figure 17, features several key components of an IGCC 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.

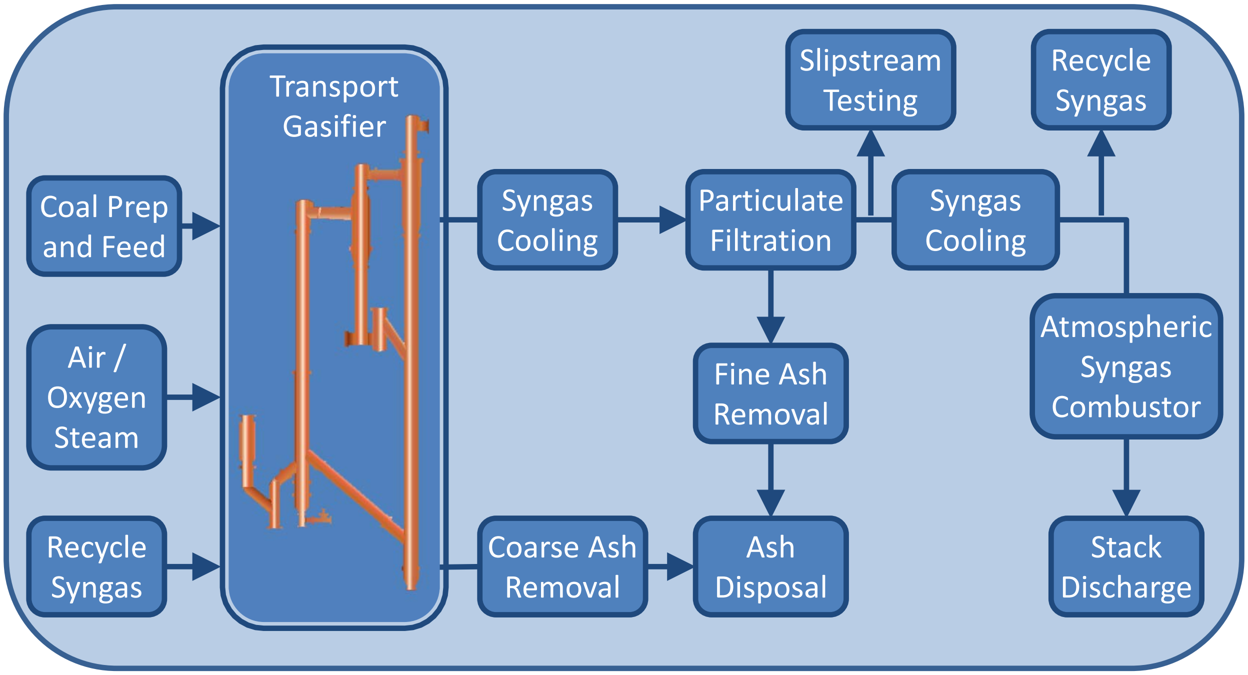

Figure 17. NCCC Gasification Process

3.1 Gasification Operation

During the reporting period, the gasification process operated in run G-1 from October 4 through November 6, 2014, for about 806 hours of operation. The test run consisted of 59 steady-state periods lasting a total of 587 hours. Many of the steady-state periods were longer than 10 hours, with some longer than 24 hours. Steady-state carbon conversion for PRB coal-only operation ranged from 97.5 to 99.9 percent and averaged 98.4 percent. Carbon conversion for the five steady-state periods achieved during biomass co-feed operation ranged from 98.6 to 99.3 percent, with an average value of 99.1 percent. Recycle syngas for gasifier aeration was used for 480 hours of the run. The newly installed primary gas cooler operated as designed and maintained an outlet temperature below 400°C throughout the run.

3.2 Hot Gas Filtration

The particulate control device operated with high collection efficiency and stable pressure drop. Although initial outlet particulate samples were contaminated with piping corrosion, subsequent sampling indicated outlet particulate loading below the sampling system detection limit of

0.1 ppmw. The filter elements, which are described in Table 6, will remain in place through the outage and the next test run.

Table 6. Hot Gas Filter Elements Tested during G-1

Filter Media Type	*Material*	*Supplier*	*Maximum Hours of Exposure*
Sintered Powder	Iron Aluminide	Pall	16,961
Fine Sintered Metal Fiber	HR-160	Pall	9,802
Coarse Sintered Metal Fiber	HR-160	Pall	11,829
Sintered Metal Powder	High alloy (SR-75)	Mott	8,307
Sintered Metal Fiber	Coated high alloy	Porvair	8,784
Sintered Metal Fiber	Fecralloy	Bekaert	3,766

3.3 SRI Fischer-Tropsch Catalyst

During G-1, SRI tested its Fischer-Tropsch reactor skid to demonstrate coal/biomass-to-liquids technology after incorporating modifications based on previous testing in run R13. The test skid consists of a gas cleanup train, a two-inch diameter F-T reactor, and a liquid product collection and sampling system. The reactor employs a selective cobalt-zeolite hybrid F-T catalyst supplied by Chevron to produce gasoline- and diesel-range hydrocarbons (C5-C20) with high productivity and selectivity. The catalyst is designed to produce clear liquid with negligible amounts of solid wax. The F-T reactor is designed to operate at nominally 21 bar using either 5 lb/hr synthetic syngas composed of hydrogen and carbon monoxide (CO) bottle gases or 3.5 lb/hr syngas from the NCCC gasifier augmented by 1.5 lb/hr bottled hydrogen and CO to achieve a hydrogen-to-CO molar ratio of 2. The test skid is designed to produce 3-4 L/day of liquid hydrocarbons.

The run was successful with about 350 hours of testing following catalyst activation. This included 184 hours with bottled syngas, followed by 69 hours with coal-derived syngas, and then by 69 hours with coal/biomass-derived syngas. After syngas operation, the catalyst was operated again with bottled gas for 24 hours, indicating no significant catalyst deactivation. The run demonstrated:

- Steady operation, efficient heat management, and nearly isothermal reactor conditions
- Efficient removal of solid tar using the gas cleaning system
- The production of greater than 2 L/day of hydrocarbon liquids
- High hydrocarbon productivity of more than four times conventional catalysts using the selective Chevron catalyst
- Wax free liquid production, low methane selectivity (less than 16.5 percent), and greater than 70 percent selectivity to gasoline- and diesel-range liquid hydrocarbons

Preliminary results indicated insignificant differences between the liquid products produced from coal and those produced from coal/biomass gasification. SRI will conduct a thorough analysis of the results, comparing coal-based results with coal/biomass-based results, and comparing the processes to a petroleum baseline.

3.4 Air Products Pressure-Swing Adsorption

Air Products conducted testing during G-1 to evaluate the performance of a two-bed sour PSA unit and to determine the stability of the PSA adsorbent. The test unit consisted of a pre-treatment skid followed by a PSA skid. The pretreatment skid contained a guard bed used to remove organic tar species from the raw syngas, a compressor to pressurize the clean sour syngas to 24 bar, and a cooler/knockout assembly to remove water and other condensable syngas components. The treated syngas was then passed to the sour PSA skid where it entered one of two PSA vessels containing adsorbent for the removal of sulfur species and CO_2.

During the regeneration steps, the bed was depressurized, purged with product gas at atmospheric pressure, and then re-pressurized with product gas. Gas exiting the bed during regeneration was characterized. The PSA product gas composition was monitored during cycling. Once stable, the inlet and outlet gas flow rates, composition, pressures, and temperatures were measured during one cycle to provide data for comparing with process simulations. The overall mass balance, hydrogen recovery, and H_2S and CO_2 rejection were then calculated. A set of breakthrough tests were also conducted before and after the PSA cycles to determine if the adsorbent properties changed during the sour syngas exposure. Breakthrough runs were conducted at 27.6 bar and 30^oC with a feed gas of 2 percent methane in helium and with 0.5 percent H_2S in helium.

The PSA operated for a total of 12 days, for 1,460 PSA cycles, on the sour syngas. The guard beds accepted sour syngas for a total of roughly 625 hours. In addition to processing sour syngas, the PSA was operated for another 560 cycles on syngas that did not contain H_2S (before breakthrough in the guard beds).

The overall mass balance was within 1 percent, while component balances were within about 8 percent. The PSA rejected 99.7 percent of the H_2S and more than 95 percent of the CO_2 in the feed gas. Product gas purity was maintained at 1.4 ppm H_2S with a feed gas concentration of around 250 ppm. The recovery of hydrogen to the product gas was 72 percent. Simulations are underway to compare the model predictions with these performance values.

The PSA system appeared to yield the same performance when similar process set points were used at the beginning and end of the sour gas testing, suggesting that the adsorbent characteristics remained stable through that period. After the syngas tests, another set of breakthrough runs were conducted, and the results showed a modest 3 percent reduction in the methane capacity and essentially no change in the H_2S capacity. These results support the observation of stable cyclic PSA performance.

3.5 Johnson Matthey Mercury Sorbent

The Johnson Matthey mercury sorbent was operated throughout the G-1 run with desulfurized, shifted syngas at a flow rate of 50 lb/hr with an operating pressure of 12.4 bar and a temperature of 260°C. NCCC gas analysis technicians took several inlet and outlet samples. No breakthrough of mercury, arsenic, or selenium was detected. The sorbent test duration was 556 hours, bringing the total testing of this material to over 4,000 hours distributed over eight gasification runs.

3.6 Water-Gas Shift and COS Hydrolysis Catalysts

The previously tested WGS catalyst and a new COS hydrolysis catalyst from the same developer were tested in G-1. For the WGS testing, about 10.6 pounds of catalyst was used in one of the SCU hot gas reactor vessels with sour syngas supplied from the hydrocarbon removal system. Continuous inlet and outlet gas analyses were used to monitor the conversion rate. Periodic measurements of the H_2S and moisture content were conducted on the outlet stream. About 270 hours of testing were conducted at six different operating conditions, with the syngas flow rate ranging from 25 to 60 lb/hr and temperatures ranging from about 200 to 250°C.

The COS hydrolysis catalyst tested was a newly developed honeycomb-shaped catalyst. The testing was conducted downstream of the developer's WGS catalyst. Gas analysis was run continuously at the vessel inlet and outlet. Table 7 provides the operating conditions for the hydrolysis catalyst and lists the average inlet and outlet COS concentration for each condition. The conversion rate averaged 39 percent.

Table 7. Operating Conditions for G-1 Testing of COS Hydrolysis Catalyst

Test Condition	Syngas Flow, lb/hr	Temperature, °C	Pressure, bar	COS Concentration, ppm	
				Inlet	Outlet
1	50	300	12.4	37	14
2	37.5	300	12.4	33	14
3	25	300	12.4	37	16
4	50	250	12.4	35	12
5	50	335	12.4	32	15
6	50	300	7.8	28	9
7	50	300	12.4	32	11

3.7 Gasification Process Modifications

Several modifications were made to the gasification process during the year to address equipment-related issues. These changes included replacement of the primary syngas cooler and repairs of damaged refractory in the gasifier seal leg found during post-R13 inspections. The refractory condition before and after repairs is shown in Figure 18.

Post-R13 Refractory Inspection

Repaired Refractory

Figure 18. Seal Leg Refractory before and after Repairs

4.0 PRE-COMBUSTION CO_2 CAPTURE

The NCCC's pre-combustion CO_2 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. The flexibility and scale of the NCCC is well suited to test CO_2 capture and gas cleanup technologies and accelerate their advancement through the component testing and pilot plant stages of development. The NCCC can test multiple projects in parallel with a wide range of test equipment sizes leading up to pre-commercial equipment sufficient to guide the design of demonstration-scale processes.

Figure 19 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. The pilot unit operates at syngas flow rates up to 1,000 lb/hr. A variety of syngas treatment steps can be implemented to meet developer requirements such as sulfur removal, trace metal removal, WGS, and hydrocarbon treatment.

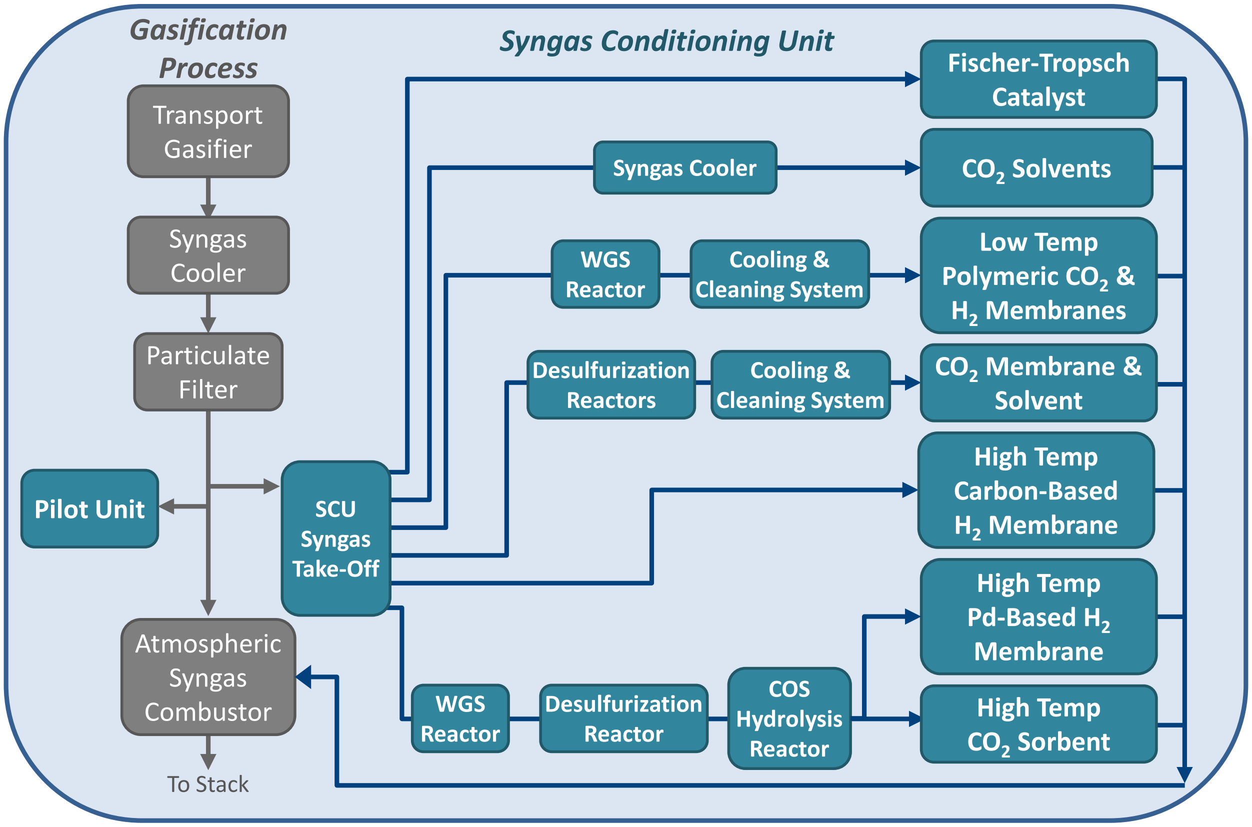

Figure 19. Schematic of Pre-Combustion CO_2 Capture Facilities

4.1 Media & Process Technology Hydrogen Membranes

The principle goal of MPT's testing of the Carbon Molecular Sieve during G-1 was to gather data on internal system behavior to be incorporated into an upgraded design for MPT's catalytic membrane reactor in series with palladium membranes. The catalytic membrane reactor combines WGS catalyst with the CMS for separation of hydrogen simultaneously with its formation.

During the G-1 run, the CMS ran approximately 100 hours on syngas, while the CMS combined with a palladium membrane ran approximately 15 hours on hydrogen-spiked syngas. For the combined system testing, the CMS membrane was able to enrich the inlet gas from about 25 percent to 75 percent. The CMS permeate was then fed to the palladium membrane, which further enriched the hydrogen content to over 99 percent.

4.2 Membrane Technology & Research Membrane

MTR participated in the G-1 run for continuation and scale-up of work on membranes previously tested at NCCC. This work was funded completely by MTR. The objectives of the test were to determine:

- Performance and stability of a four-inch commercial-sized Proteus membrane module (having a surface area of 1 to 4 m^2) on the pilot-scale 50 lb/hr syngas separation skid at a temperature of 120°C
- Syngas separation performance and stability of Generation 2 (Gen-2) Proteus membranes stamps (each with a surface area of 30 cm^2) at temperatures up to 200°C

The pilot-scale system was originally designed to test the performance of CO_2-selective Polaris^{TM} membrane modules and Proteus membrane stamps, and was installed in September 2009. It has been used continuously to evaluate the separation performance and long-term stability of new membranes and modules as they have become available from parallel off-site optimization and improvement activities. Prior to run R12, the skid was modified to run at elevated temperatures (150°C), in order to test commercial-size Proteus modules. An indirect gas heater was installed, and the entire skid was heat-traced and insulated. However, issues with poor skid temperature control during the R12 run led to lower than expected module performance. Prior to the start of the R13 run, additional heat tracing was installed on the feed and vessel sections of the skid, and the heat tracing sensors were relocated. For the G-1 run, the location of the vessel heat tracing temperature sensor was moved to the center of the vessel to more accurately measure the module temperature during testing.

Test Results for Four-Inch Proteus Membrane Module

A single four-inch Proteus membrane module was used for the entire run to measure membrane performance, long-term stability, and the effect of high-temperature syngas conditions on module components (spacers, glue lines, etc.). The skid temperature set point was 120°C for the duration of the run. Figure 20 shows the hydrogen concentration in the feed and permeate streams of the pilot-scale skid for the duration of run. The hydrogen concentration was enriched in the permeate to approximately three to four times the feed concentration, which is consistent with the previous Proteus module results from testing in 2014.

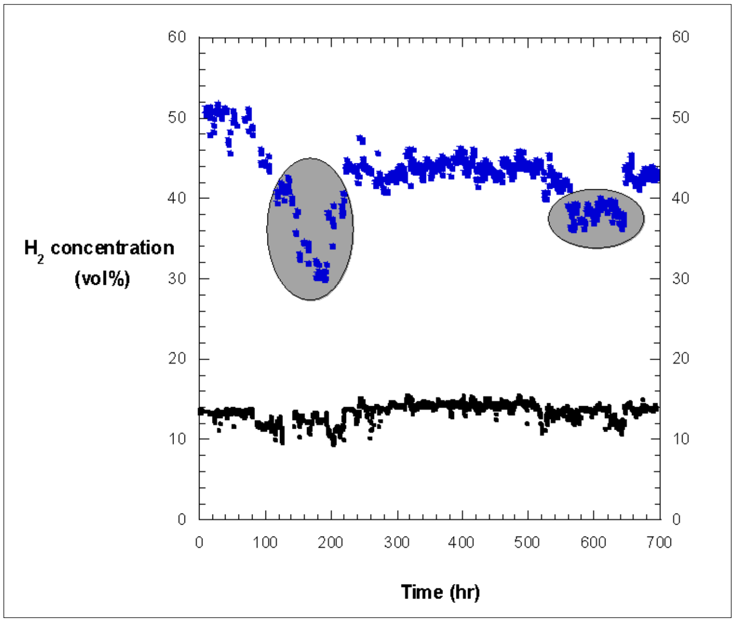

Figure 20. Hydrogen Concentration in the Feed and Permeate Streams of MTR Proteus Membrane Module during G-1

Some annealing or densification of the Proteus membrane is expected during the beginning of the campaign when the membrane module is first exposed to elevated temperatures. This is reflected in the reduction in the hydrogen permeate concentration during approximately the first 100 hours of testing. In the test time between approximately 120 hours and 240 hours (highlighted by the left gray oval in Figure 20), various operating parameters outside of the normal range led to reduced module performance. During this time, the skid was operating at a reduced flow rate (due to catalyst testing upstream of the MTR skid), which caused the skid to operate at a higher than ideal module stage-cut. For a portion of this time, the skid was also running at temperatures lower than 120°C, which led to reduced hydrogen permeance values. The final detrimental condition was plugging of the permeate orifice plate, which led to artificially high permeate pressures and therefore a reduced driving force for hydrogen permeation. The permeate orifice plate was also plugged between approximately 520 and 650 hours (as shown in the smaller, right gray oval in Figure 20), resulting in an appreciably lower hydrogen concentration in the permeate stream. When all operating parameters were within normal ranges, the permeate hydrogen concentration was consistently in the range of 40 to 45 vol% during the last 450 hours of testing.

Test Results for Gen-2 Proteus Membrane Stamps

First generation (Gen-1) Proteus membranes showed good hydrogen permeance and selectivity characteristics with syngas operation during previous NCCC runs. However, the inherent thermal stability of Gen-1 Proteus membranes restricts their operating temperature to less than

170°C. Since the outlet stream of a WGS reactor is typically about 200°C, it is desirable to have a membrane capable of operating at this temperature while still delivering hydrogen permeance and selectivity performance similar to Gen-1 Proteus.

Gen-2 bench-scale Proteus membranes were developed specifically for higher temperature operation. These newly developed membranes showed good stability and hydrogen separation characteristics at temperatures up to 200°C during MTR's preliminary lab testing. The first test of Gen-2 Proteus membranes under real syngas feed conditions was during run R13. Sulfur-containing syngas was fed to two Gen-2 Proteus stamps operated in series for approximately 330 hours. Over that period, the temperature was varied from 118°C to 140°C, and the membrane stability and hydrogen separation performance were evaluated. Early shutdown of the R13 run prevented membrane performance at higher temperatures from being investigated.

The goal of the Gen-2 stamp tests during the G-1 run was to investigate separation performance and stability with sulfur-containing syngas at temperatures from 140°C to 200°C. The feed and permeate hydrogen concentrations during the stamp test are plotted in Figure 21. The hydrogen permeate concentration at 140°C (from 0 to 160 hours) was not consistent with that measured during R13 (80 to 85 vol%), and the concentration at 160°C was also lower than anticipated. A check valve that prevents back flow from the residue to the permeate was suspected to be faulty, resulting in low and highly fluctuating measurement of the permeate hydrogen concentration and permeate pressure. At approximately 300 hours, the permeate stream was isolated from the residue by closing a blocking valve and sending the entire permeate flow to the gas chromatograph. The measured permeate hydrogen concentration stabilized and was consistent with anticipated values after closing the blocking valve. The Gen-2 stamps showed good stability at 180°C and 194°C while still maintaining excellent hydrogen separation performance.

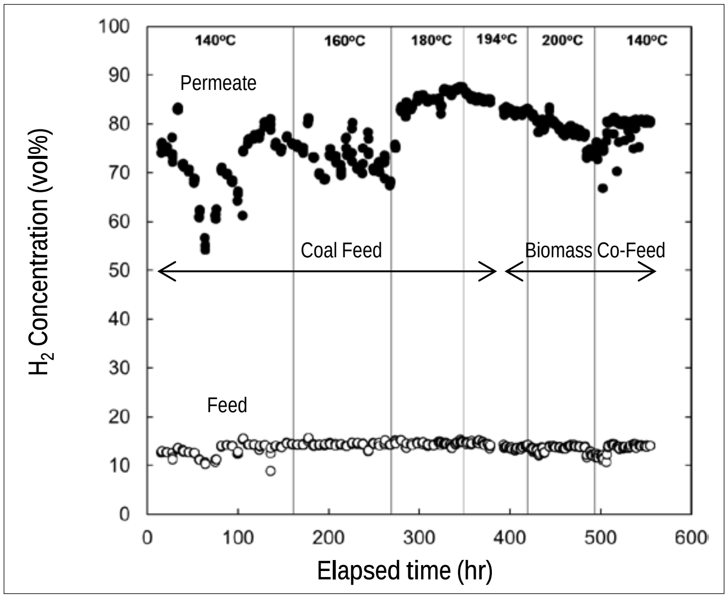

Figure 21. Hydrogen Concentration in the Feed and Permeate Streams of MTR Gen-2 Proteus Stamp Cell Unit during G-1

Table 8 summarizes the calculated average permeance and selectivity values for the Gen-2 Proteus membranes. Permeance and selectivity values for the first 270 hours were not included in this table because of the high degree of variance in permeate flow and composition measurements during that period. The best Gen-2 performance was measured at a feed temperature of 180°C, at which the hydrogen permeance and H_2/CO_2 selectivity were calculated to be 200 gpu and 22, respectively. After elevating the feed temperature to 194°C, the H_2/CO_2 selectivity was reduced to 19 while hydrogen permeance remained at 200 gpu. Relative to the values calculated at 180°C and 194°C, all gas permeance and H_2/gas selectivity values at 200°C were further reduced, suggesting that membrane densification and/or degradation occurred at the higher temperature.

Table 8. Average Permeance and Selectivity for Gen-2 Proteus Stamps Tested in G-1

Feed Temp. (Oven Temp. Setpoint), °C	Permeance, gpu				Selectivity		
	H_2	CO_2	N_2	CO	H_2/CO_2	H_2/N_2	H_2/CO
180 (189)	200	9.3	2.0	2.6	22	110	70
194 (204)	200	10	1.8	2.6	19	110	76
200 (209)	120	7.7	1.4	2.1	15	79	55

Future work planned by MTR includes post-test analysis of the stamps tested during G-1 and continuation of high-temperature stability studies to further define the upper limit of operation. MTR plans to continue supporting both types of testing with MTR internal funds during the next NCCC gasifier run in 2015.

5.0 CONCLUSIONS AND LESSONS LEARNED

5.1 Post-Combustion

Cansolv Technologies Solvent

The PSTU was operated with two solvents from Cansolv Technologies at expected commercial operating conditions at 90 percent CO_2 capture. During operation, the ELPI+ instrument was used to measure flue gas aerosol and particulate concentrations.

MEA Solvent for DOE Carbon Capture Simulation Initiative

The PSTU was operated for more than 400 hours with MEA to provide data for computer model validation. Dynamic and parametric testing was completed.

University of Edinburgh Solvent Analyzer

During the MEA operation, testing of a novel solvent analyzer was completed to support development of real-time instrumentation for future carbon capture plants.

DOE C2U Sorbent Unit

Operation of DOE's C2U in both circulating and batch modes was conducted for evaluation of heavy metals accumulation. Post-operation analyses showed no permanent loss of CO_2 capture capacity. Due to the possibility of trace elements being removed from the flue gas upstream of the sorbent, chemical analysis of the inlet flue gas stream is recommended to better gauge trace element accumulation.

SRI International Sorbent

Testing with the SRII sorbent skid was completed to support technology scale-up. The pneumatic lift of the sorbent microbeads is not the preferred design for the pilot-scale unit. A bucket elevator will be used to lift the sorbent microbeads. SRII's determinations included:

- Successful use of pinch valves to control the flow of the sorbent microbeads
- The need for increased heat exchanger tube density
- The need for preheating the sorbent microbeads to minimize steam injection
- Effective sorbent bead separation with multiple layers of packing
- High heat losses of the bench-scale unit, with higher heat efficiency expected for scale-ups

Membrane Technology & Research 1-TPD Membrane System

MTR continued operation of the 1-TPD system for membrane design evaluations. The membrane modules tested showed comparable CO_2 enrichment rates, but varying CO_2 removal rates.

Membrane Technology & Research 20-TPD Membrane System

MTR operated the 20-TPD system for the first time, and completed all testing by the end of the reporting period. Operation improved during the second run, and MTR successfully demonstrated a four-fold reduction in pressure drop with the plate-and-frame sweep module in comparison to the spiral module used in the first run.

Ohio State University Membranes

OSU began testing a bench-scale membrane unit, with operation to be completed in June 2015.

Linde-BASF Solvent Process

Results showed that a 90 percent CO_2 capture rate is easily achieved, with the capture rate adjustable by changing the steam flow rate. A CO_2 product purity of 99.9 percent on a dry basis was typically achieved during the tests.

Carbon Capture Scientific Gas-Pressurized Stripping Process

CCSp's bench-scale process demonstrated over 95 percent CO_2 capture with over 95 percent CO_2 product purity. The fluctuation of solvent water concentration resulting from changing ambient temperatures influenced the performance of the overall process and necessitated the periodic addition of make-up solvent.

PC4 Upgrades

To meet the requirements of future testing at the PC4, work was completed in increasing the plant capacity. Modifications were made to the PSTU to increase space for technology developer equipment and to improve data acquisition. Work also continued on the SSTU, with final modifications identified.

5.2 Gasification

Gasification Operation

The gasification process operated in run G-1 for 806 hours in October and November of 2014. Fuels used included PRB coal and biomass. Operation was stable, with high carbon conversions and consistent quality syngas for use in gasification and pre-combustion tests.

Hot Gas Filtration

Research efforts continued during the year for the long-term evaluation of material performance of several types of filter elements. The elements installed continued to demonstrate excellent filtration efficiency.

Southern Research Institute Fischer-Tropsch Catalyst

SRI's Fischer-Tropsch reactor skid operated successfully after incorporating modifications based on previous testing. After syngas operation, the catalyst was operated again with bottled gas for 24 hours, indicating no significant catalyst deactivation. The run demonstrated high hydrocarbon productivity of more than four times conventional catalysts using the selective Chevron catalyst.

Air Products Pressure-Swing Adsorption

The PSA operated for a total of 12 days, for 1,460 PSA cycles, on sour syngas. The overall mass balance was within 1 percent, while component balances were within about 8 percent. The PSA rejected 99.7 percent of the H_2S and more than 95 percent of the CO_2 in the feed gas. The system appeared to yield the same performance when similar process set points were used at the beginning and end of the sour gas testing, suggesting that the adsorbent characteristics remained stable through that period.

Johnson Matthey Mercury Sorbent

During the sorbent testing, no breakthrough of mercury, arsenic, or selenium was detected. The sorbent test duration was 556 hours, bringing the total testing of this material to over 4,000 hours distributed over eight gasification runs.

Water-Gas Shift and Carbonyl Sulfide Hydrolysis Catalysts

The previously tested WGS catalyst and a new COS hydrolysis catalyst from the same developer were tested in G-1. The WGS catalyst continued to demonstrate long-term stability, and the COS hydrolysis catalyst demonstrated a 39 percent conversion rate.

5.3 Pre-Combustion

Media & Process Technology Hydrogen Membrane

MPT's CMS ran approximately 100 hours on syngas, while the CMS combined with a palladium membrane ran approximately 15 hours on hydrogen-spiked syngas. For the combined system testing, the CMS membrane was able to enrich the inlet gas from about 25 percent to 75 percent. The CMS permeate was then fed to the palladium membrane, which further enriched the hydrogen content to over 99 percent.

Membrane Technology & Research 50-lb/hr Hydrogen Membrane

The hydrogen concentration was enriched in the permeate to approximately three to four times the feed concentration, which is consistent with the previous Proteus module results from testing in 2014. When all operating parameters were within normal ranges, the permeate hydrogen concentration was consistently in the range of 40 to 45 vol% during the last 450 hours of testing.

Membrane Technology & Research Hydrogen Membrane Stamp Cells

The best Gen-2 performance was measured at a feed temperature of 180°C, at which the hydrogen permeance and H_2/CO_2 selectivity were calculated to be 200 gpu and 22, respectively. After elevating the feed temperature to 194°C, the H_2/CO_2 selectivity was reduced to 19 while hydrogen permeance remained at 200 gpu. Relative to the values calculated at 180°C and 194°C, all gas permeance and H_2/gas selectivity values at 200°C were further reduced, suggesting that membrane densification and/or degradation occurred at the higher temperature.