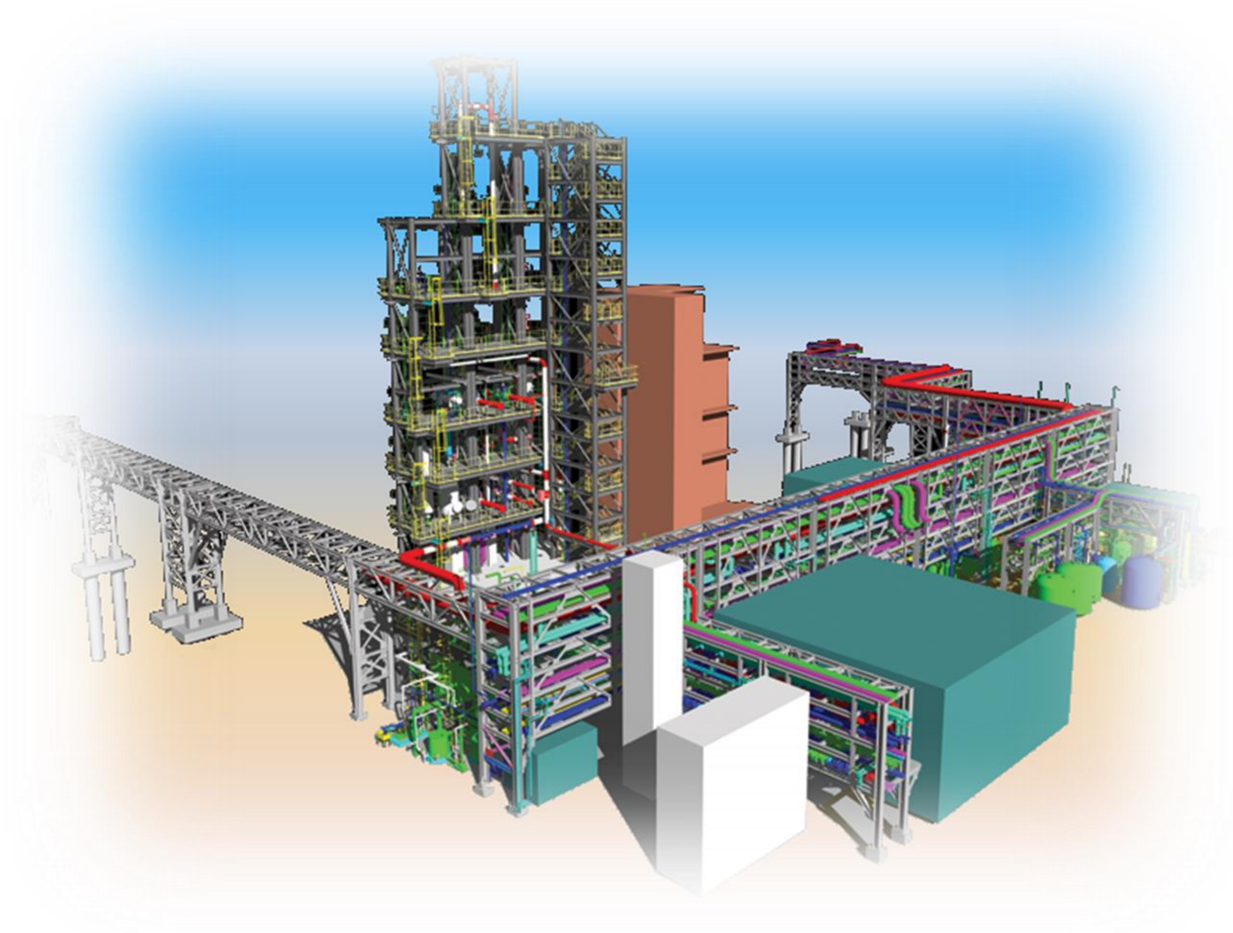
The National Carbon Capture Center at the Power Systems Development Facility

Topical Report

Budget Period Four

January 1, 2013 – December 31, 2013



DOE Cooperative Agreement
DE-NT0000749

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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 technologies for CO_2 capture from coal-derived flue gas and syngas.

The NCCC includes multiple, adaptable test skids 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 paths to commercialization.

During the calendar year 2013 portion of the Budget Period Four reporting period, efforts at the NCCC focused on post-combustion CO_2 capture, gasification, and pre-combustion CO_2 capture technology testing. Preparations for future testing were on-going as well, and involved facility upgrades and collaboration with numerous technology developers.

In the area of post-combustion, testing was conducted on an enzyme-based technology, advanced solvents from two major developers, and a gas separation membrane. During the year, the gasification process was operated for three test runs, supporting development of water-gas shift and COS hydrolysis catalysts, a mercury sorbent, and several gasification support technologies. Syngas produced during gasification operation was also used for pre-combustion capture technologies, including gas separation membranes from three different technology developers, a CO_2 sorbent, and CO_2 solvents.

Acknowledgement

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List of Abbreviations and Acronyms

CFM	Cross-Flow Membrane
CMR	Catalytic Membrane Reactor
CMS	Carbon Molecular Sieve
COS	Carbonyl Sulfide
CSM	Countercurrent-Swept Membrane
DEPG	Dimethyl Ether of Polyethylene Glycol
DMI	Dimethylimadizole
DOE	Department of Energy
EPA	Environmental Protections Agency
FEAL	Iron Aluminide
GTA	Glycerol Triacetate
H_2S	Hydrogen Sulfide
HSX	Hybrid Siloxane
IGCC	Integrated Gasification Combined Cycle
MCC	Motor Control Center
MEA	Monoethanolamine
MEI	Methylimidazole
MM5	Modified Method 5
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
PCC	Post-Combustion CO_2 Capture
PCD	Particulate Control Device
PDMS	Polydimethyl Siloxane
PRB	Powder River Basin
PSDF	Power Systems Development Facility
PSTU	Pilot Solvent Test Unit
SCL	Syngas Chemical Looping
SCU	Syngas Conditioning Unit
SRII	SRI International
SSTU	Slipstream Solvent Test Unit
TPD	Ton per Day
UA	University of Alabama
WGS	Water-Gas Shift
WPI	Worcester Polytechnic Institute

1.0 EXECUTIVE SUMMARY

The Power Systems Development Facility (PSDF) is a key national asset for ensuring continued cost-effective, environmentally acceptable energy production from coal. Sponsored by the U.S. Department of Energy's (DOE's) National Energy Technology Laboratory (NETL), the PSDF is an engineering scale test center located in Wilsonville, Alabama. The PSDF staff has effectively developed advanced power systems to meet the national need for cleaner, more efficient power production from coal. In the 18 years of PSDF operation, numerous technologies have been tested under challenging process conditions without any lost-time accidents.

Building on its previous success, PSDF now houses the National Carbon Capture Center (NCCC), established in 2009. The NCCC provides test facilities and wide-ranging support to researchers developing lower-cost CO_2 capture technologies that will enable coal-based power generation to remain a key contributor to the energy mix. The facilities accommodate a range of equipment sizes and operating conditions and provide commercially representative settings that allow results to be scaled confidently to commercial application, a crucial element in shortening development times.

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 in 1996, the PSDF has been a center for national efforts to develop clean, high efficiency coal-based power generation technologies. Two significant achievements–in addition to many secondary goals that were met–were the development of hot gas filtration to improve energy efficiency and the development of a gasifier suitable for use with low-rank coals, which comprise over half of the total coal reserves in the U.S. and the world. These two technologies have progressed to commercialization with an integrated gasification combined cycle (IGCC) power plant under construction in Kemper County, Mississippi.

Project Mission and Approach

Offering a world-class neutral test facility and a highly specialized staff, the National Carbon Capture Center 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

1.1 Post-Combustion CO_2 Capture Accomplishments

During the year, the PC4 achieved over 10,000 hours of operation despite being off-line during two major outages of Gaston Unit 5. The PC4 has operated for a total of about 22,800 hours to date and has incorporated several upgrades to accommodate future testing. Highlights of the 2013 accomplishments are listed below.

- Enzyme Testing—With more than 3,500 hours of operation, Akermin successfully confirmed proof-of-concept of its pilot-scale process featuring immobilized carbonic anhydrase enzymes using a potassium carbonate solvent and an amine solvent. The testing demonstrated over 90 percent CO_2 capture with significantly lowered energy costs, and the data provided a well-defined path for Akermin to further optimize system performance to achieve as much as 15-fold acceleration of CO_2 capture.

- Solvent Testing—The PSTU operated for more than 3,000 hours with amine solvents from two developers, Chiyoda and Cansolv, providing critical data in support of scale-up to commercial demonstrations. Both test campaigns required modifications to the PSTU (solvent recycling and solvent carryover reduction measures for Chiyoda and an air dilution system to simulate natural gas-fired conditions for Cansolv) to produce data that is representative of each developer's planned commercial operation. Both solvents achieved over 90 percent CO_2 capture, and the developers are assessing other key performance indicators, such as solvent degradation rates and corrosion characteristics.
- Membrane Testing—Membrane Technology & Research (MTR) refined its 1-ton CO_2/day membrane process by incorporating new designs for membrane modules and optimizing operation with a new compressor. MTR operated the process for over 3,500 hours on flue gas during the year with stable membrane performance, and preparations continued for operation of the scaled-up, 20-ton/day system in 2014.
- Initial Sorbent Testing—The SRI International sorbent skid was installed at the PC4 and commissioned with flue gas. Testing of the novel sorbent technology will be completed in 2014.
- Preparations for Pilot Demonstration of Solvent Process—The NCCC completed site preparations and utility connections for the Linde-BASF solvent unit, which is to be installed and tested in 2014.
- Balance-of-Plant Upgrades—A new cooling tower, electrical infrastructure, flue gas blower, and pre-scrubber components were installed. These additions, along with others being completed in 2014, will increase the total PC4 capacity from 12,000 lb/hr of flue gas to about 30,000 lb/hr, allowing simultaneous operation of pilot units.

1.2 Gasification Technology Accomplishments

The gasification process operated in three different test runs, R10, R11, and R12, for more than 2,000 hours in 2013, bringing the total gasification operational hours to over 20,000. The syngas produced was utilized for the development of several gasification support processes as well as for pre-combustion CO_2 capture technologies. Accomplishments in the area of gasification testing include:

- Long-Term Evaluations—Enhancements made on automatic gasifier controls were successful in modulating gasifier temperature with high moisture lignite operation, supporting the goal of fuel diversity with the Transport Gasifier. Coal feeder level probes used to control the developmental coal feeder continued to demonstrate reliable operation. Long-term studies of high efficiency particulate filter elements have demonstrated excellent filtration performance over an expected two-year commercial service for the most extensively tested elements at the NCCC.
- Gasifier Instrumentation—Testing was conducted with a sapphire thermowell in gasifier service, which was modified by the vendor based on past operation at the site. The

ongoing collaboration of the vendor and NCCC staff resulted in significantly improved performance without the previously occurring degradation of the sapphire thermowell-housed thermocouple.

- Mercury Sorbent—Operation of Johnson Matthey's high temperature mercury sorbent continued, using a newly installed reactor for higher syngas throughput. The sorbent continued to demonstrate excellent capture performance and promise as a high efficiency alternative to conventional mercury capture technology.
- Water-Gas Shift (WGS) and Carbonyl Sulfide (COS) Hydrolysis Catalysts—Parametric and long-term testing of a developmental WGS catalyst was ongoing throughout the year. The catalyst demonstrated CO conversions equal to or greater than equilibrium values without steam addition. The catalyst developer also supplied a new COS hydrolysis catalyst that was tested for the first time in R12, with long-term evaluation planned for this catalyst as well.
- Syngas Chemical Looping—The Ohio State University (OSU) Syngas Chemical Looping (SCL) pilot-scale process was installed, and initial commissioning began. This novel process will be demonstrated with syngas operation in 2014.

1.3 Pre-Combustion CO_2 Capture Accomplishments

Pre-combustion CO_2 capture testing during the year included more than 4,500 hours of membrane and sorbent operation. Testing also included characterization of physical solvents with bottle gas and with syngas during gasification runs. Highlights in the area of pre-combustion CO_2 capture are given below.

- Hydrogen Membranes—The three hydrogen membrane developers testing in 2013, MTR, Media & Process Technology (MPT), and Worcester Polytechnic Institute (WPI), have been actively scaling up their processes based on NCCC test results. For R12, MTR converted its 50 lb/hr CO_2 membrane system to test hydrogen membranes, which had previously been tested at a 1-lb/hr scale. MPT successfully converted its 50 lb/hr hydrogen membrane module to a catalytic membrane reactor in R10 by adding water-gas shift catalyst, providing separation of hydrogen simultaneously with its formation. WPI continued development of palladium-based membranes with a 10-lb/hr unit and is in the process of designing a 50-lb/hr unit.
- CO_2 Membrane—MTR continued testing of its scaled-up, integrated membrane system that was first operated in late 2012. System operation in R10 and R11 showed marked improvement and demonstrated high purity liquid CO_2 production.
- CO_2 Sorbent Testing—TDA Research first tested a solid CO_2 sorbent in 2011 and returned in R10 for further testing with added water-gas shift functionality. R10 results showed that greater than 96 percent CO conversions were possible at steam-to-CO ratios of less than 1.2 and that CO_2 capture efficiency was 96 percent or greater.
- CO_2 Solvent Testing—Solvents previously tested only with bottle gas in lab settings from the University of Alabama and from DOE's NETL were fully characterized with syngas

operation. The solvent runs were conducted at established baseline conditions to allow comparisons to all the solvents tested at the site.

- Syngas Conditioning Unit (SCU) Enhancements—The NCCC continued upgrades to the SCU, which houses the pre-combustion CO_2 capture test skids and support infrastructure. The newly installed, high capacity syngas cleaning system was optimized based on initial operation, and new WGS and COS hydrolysis reactor vessels were added.

1.4 Milestones for 2013

The Budget Period Four performance period for the NCCC entails a total period of 33 months, from January 2012 through September 2014. This report describes the results of work at the NCCC for the calendar year 2013 portion of Budget Period Four. In partnership with the DOE, the NCCC established and met the milestones listed in during 2013.

Table 1. Major Project Milestones for the 2013 Portion of Budget Period Four

Research Area	*Milestone*	*Completion Date*	*Report Section*
Gasification	Start gasification test run R10: 750 hours of on-coal operation with PRB; testing of mercury sorbent	Mar 2013	3.0
Pre-Combustion	In R10 test CO_2 solvent in batch reactor; TDA CO_2 sorbent; membranes from MTR, MPT, or WPI; a large-scale membrane from MTR; and WGS catalyst	Mar 2013	4.0
Gasification	Complete micropile work for OSU SCL foundations	Mar 2013	3.6
Post-Combustion	Complete testing of Chiyoda solvent in PSTU	Mar 2013	2.2
Post-Combustion	Test Akermin enzyme-based process in bench-scale area	Mar 2013	2.1
Post Combustion	Continue testing MTR membrane in bench-scale area	Mar 2013	2.4
Gasification / Pre-Combustion	Complete gasification test run R10 and associated pre-combustion tests begun in previous quarter	Apr 2013	3.1, 4.0
Post Combustion	Test Akermin enzyme-based process in bench-scale area	Jun 2013	2.1
Post Combustion	Continue testing MTR membrane in bench-scale area	Jun 2013	3.1
Post Combustion	Begin Cansolv solvent test in PSTU on simulated NG flue gas	July 2013	3.1
Post Combustion	Install foundations to support Linde solvent test skid	May 2013	2.7
Gasification	Conduct gasification test run R11: 750 hours of on-coal operation with lignite; testing of mercury sorbent	Aug 2013	3.1
Pre-Combustion	In R11 test CO_2 solvent; membranes from MTR, MPT, WPI, or other; large-scale MTR membrane; and WGS catalyst	Aug 2013	2.4
Pre-Combustion	Install a new syngas slipstream, steam, and compressed air lines to support OSU's SCL field demonstration	Sept 2013	3.6
Post Combustion	Continue testing MTR membrane in bench-scale area	Sept 2013	2.4
Post Combustion	Extend testing of Akermin process	Oct 2013	2.1
Post Combustion	Complete Cansolv solvent test in PSTU on simulated NG flue gas	Oct 2013	2.3
Gasification	Conduct gasification test run R12: 750 hours of on-coal operation with PRB; commission OSU's SCL	Dec 2013	3.1
Pre-Combustion	In R12 test DOE CO_2 solvent; MTR, MPT, WPI, or other membranes; WGS and COS hydrolysis catalysts	Dec 2013	2.4
Post Combustion	Begin SRI International sorbent test in bench-scale area	Oct 2013	2.5
Post Combustion	Continue testing MTR membrane in bench-scale area	Dec 2013	2.4

2.0 POST-COMBUSTION CO_2 CAPTURE

The PC4 advances flue gas CO_2 capture processes at a range of operating conditions and technology development stages. As illustrated in Figure 2, the PC4 features the PSTU for solvent testing at up to 0.5 MWe, test bays for larger units up to 1.0 MWe, and areas for bench-scale units up to 0.1 MWe each. The site also includes an independent control room, electrical infrastructure, and a balance of plant area containing utilities and chemical storage/handling facilities.

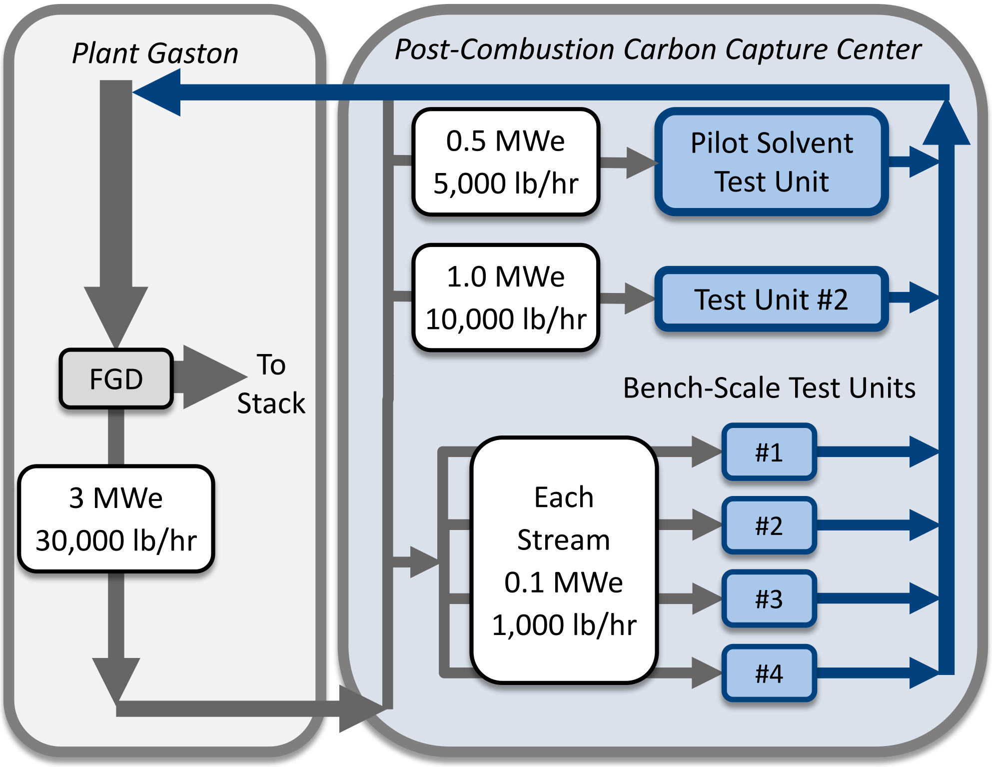


Figure 2. PC4 Facilities

In early 2013, the NCCC implemented modifications to the PSTU to accommodate Cansolv's natural gas combined cycle flue gas simulation test. Piping was added to introduce air into the flue gas leaving the pre-scrubber to lower the CO_2 from about 12 vol% to as low as 4 vol%, comparable to natural gas flue gas. For operation at this lower CO_2 concentration, the flue gas flow was increased. Additional flow meters and pumps were installed in parallel with the existing equipment items to allow switching between the two operating modes. During testing of the Cansolv solvent with the natural gas simulated flue gas, the other developers testing at the PC4 necessarily operated with this diluted flue gas.

2.1 Akermin Enzymes

Akermin has been developing immobilization/stabilization systems to deploy carbonic anhydrase enzyme into the absorber of commercial gas-liquid contactor systems to accelerate the capture of CO_2 in widely available low-cost commodity base chemicals. For example, unlike most amine solvents, potassium carbonate is non-volatile, does not degrade in the presence of oxygen, SO_2 and other impurities, and has low corrosion potential. These properties eliminate the cost of wash towers and solvent clean up equipment, eliminates VOC emission potentials, and eliminates the need for corrosion inhibitors. While the heat of reaction is nearly one third that of monoethanolamine (MEA), capture rates in potassium carbonate are much slower. Indeed, potassium carbonate does not react directly with carbon dioxide in the same way as MEA. Instead, CO_2 is first hydrated with water before the base completes the reaction, as shown in the chemical equations below. While CO_2 hydration is slow in the absence of catalyst, carbonic anhydrase is a very efficient catalyst for this reaction (kcat ~ 10^6/s). Therefore, developing and demonstrating enzyme-catalyzed technology is beneficial to the program to enable non-volatile and non-toxic solvents with potentials to reduce cost of capture.

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad \text{(catalyst needed)}$$

$$H^+ + B \leftrightarrow BH^+ \qquad \text{(fast)}$$

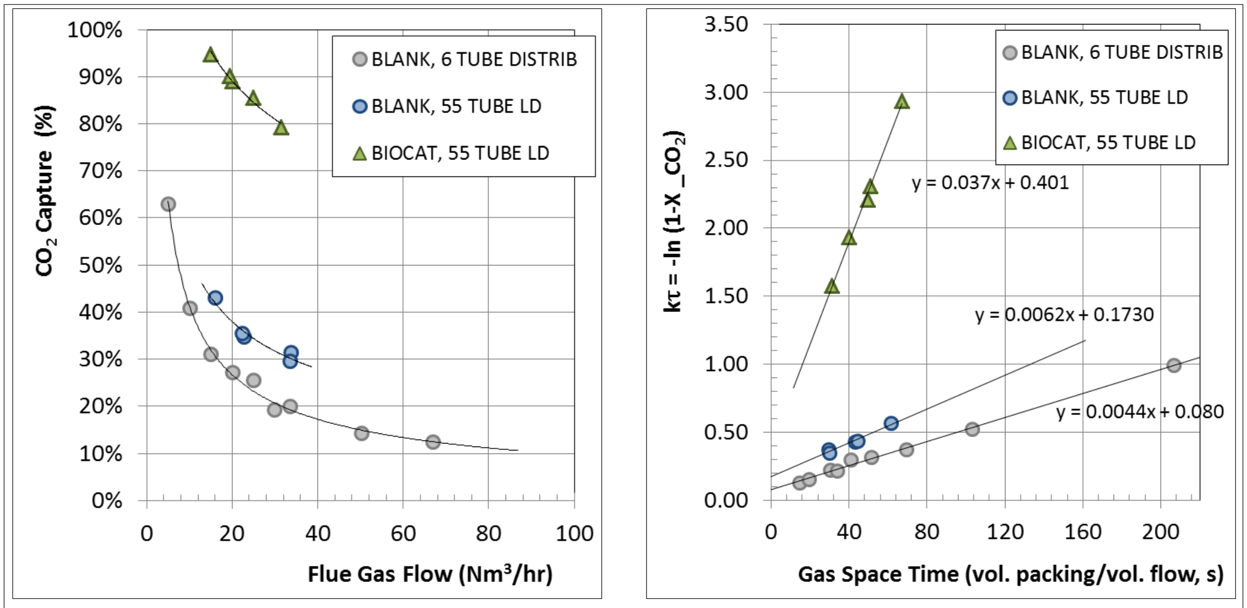
$$CO_2 + H_2O + B \leftrightarrow HCO_3^- + BH^+ \qquad \text{(overall reaction)}$$

Akermin's proof of concept enzyme delivery system used active enzyme encapsulated in a thin polymer film that was subsequently deposited on the surface of the absorber packing. In this case, the enzyme is immobilized on the packing material. This avoids transferring the enzyme into the high-temperature stripper column where it can potentially become thermally inactivated.

From March through September, Akermin completed approximately 2,800 operational hours on flue gas with minimal decline in the performance of the biocatalyst. Around 1,500 hours were completed with undiluted flue gas (12 percent CO_2) with the remainder on simulated natural gas flue gas (4 percent CO_2). Reliable operation was demonstrated, operating availability being 99 percent relative to flue gas supply.

During this time, operation with the carbonic anhydrase enzymes demonstrated 90 percent CO_2 capture and produced a regenerated CO_2 stream with 99.9 percent purity. Heat stable salt accumulation was negligible. Unlike operation with amine-based solvents, solvent carryover was below detection limits, with less than 1.6 percent per year capacity loss due to heat stable salts. Comparatively, previous MEA testing at the NCCC has demonstrated that up to 0.5 percent of solvent can be lost in a day due to volatility and aerosol formation alone.

Figure 3 presents test data with the immobilized enzyme data compared to data with blanks using the same liquid distributor with 55 tubes and with blanks in a 6-tube distributor. Data presented in Figure 3 were collected at various gas flow rates with a constant liquid-to-gas ratio and constant lean loading. It was shown that a first order plot gives a linear presentation of the CO_2 capture data with varied space time. Data demonstrated that a seven-fold increase in flue gas flow rate was possible while maintaining 90 percent CO_2 capture in the same column with enzyme operation and a six-fold increase in the mass transfer coefficient.



CO_2 Capture

First Order Plot

Figure 3. CO_2 Capture and Reaction Kinetics with and without Akermin Enzymes

Beginning in October, Akermin extended operation of the enzyme system, replacing potassium carbonate solvent with a proprietary amine solvent, AKM-24, as indicated in Figure 4. The data represents operation at constant conditions with a gas flow rate of 31.5 Nm^3/hr, a liquid flow rate of 275 L/hr, and lean loading at 0.25 mol/mol, demonstrating stable enzyme performance.

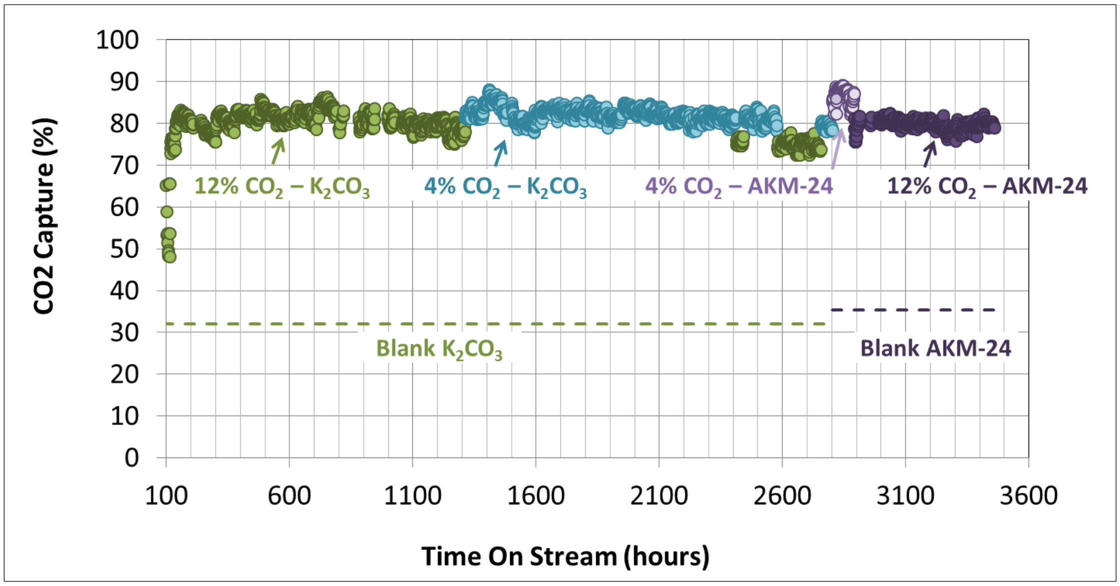


Figure 4. CO_2 Capture over Time at Constant Gas and Liquid Flow Rates and Lean Loading

Approximately 713 hours were achieved with the AKM-24 solvent, including 578 hours with typical flue gas and 135 hours with natural gas-simulated flue gas. The CO_2 capture efficiency was around 80 to 90 percent at design conditions.

In conclusion, Akermin completed a successful test campaign at PC4 with more than 3,500 hours testing the immobilized carbonic anhydrase enzyme-based system. Testing demonstrated:

- More than 2,800 hours on coal flue gas with an average steady performance of about 80 percent CO_2 capture using potassium carbonate solvent
- 700 hours of operation with the AKM-24 solvent, with 80 to 90 percent capture at design conditions and demonstrating stable performance
- Low solvent loss due to essentially zero volatility and also low heat stable salt build up (less than 1.6 percent per year capacity loss due to heat stable salts)
- Aerosol emissions lower than detection limit of 0.8 ppm
- High purity (greater than 99 percent) CO_2 production
- Negligible detectible corrosion rates using 304-stainless steel
- Energy consumption of about 3.5 GJ/ton CO_2 with the Akermin process using potassium carbonate

2.2 Chiyoda Solvent

Based on its experience as a worldwide engineering, procurement, and construction contractor, the Chiyoda Corporation is focusing on suitable commercial plant designs for low carbon emissions. As part of this effort, Chiyoda has been developing an advanced amine solvent in conjunction with an optimized CO_2 capture process. After equipment modifications to the PSTU requested by Chiyoda were completed, testing of the T-3 solvent began in December 2012. Chiyoda completed testing in June 2013, for about 1,500 hours of operation.

Operation with the Chiyoda solvent included 24 test conditions, and mass balances were completed for each condition with 97 percent or higher closures. Chiyoda is completing data analysis and will report the results once finalized.

2.3 Cansolv Technologies Solvent

As part of its research and development of CO_2 capture processes, Cansolv Technologies conducted extensive testing of its DC-201 solvent in the PSTU in 2012. Testing involved parametric studies, equipment configurations, and solvent additives. In 2013, Cansolv augmented the previous testing with operation using flue gas diluted with air to simulate natural gas-fired operations. Testing commenced on July 11, and the initial tests varied the liquid-to-gas ratio in the absorber and steam flow rates to the regenerator to optimize operating. Long-term testing was focused on solvent performance, degradation, and emissions. Cansolv concluded the successful test campaign on October 7, with 1,715 hours of operation with natural gas simulated flue gas.

2.3.1 Operation and Results

The CO_2 removal and stripping factor versus total transformation products are shown in Figure 5 and Figure 6, respectively. These parameters were plotted against total transformation products to provide a clear indication of how the solvent performs at different stages of the piloting campaign. Throughout the campaign, overall CO_2 capture performance did not deteriorate significantly as transformation products increased in concentration, since the DC201 solvent transformation products maintain a certain strong capacity for capturing CO_2. The results in Figure 5 demonstrate no noticeable loss of CO_2 capture performance before a total transformation concentration near the middle of the test.

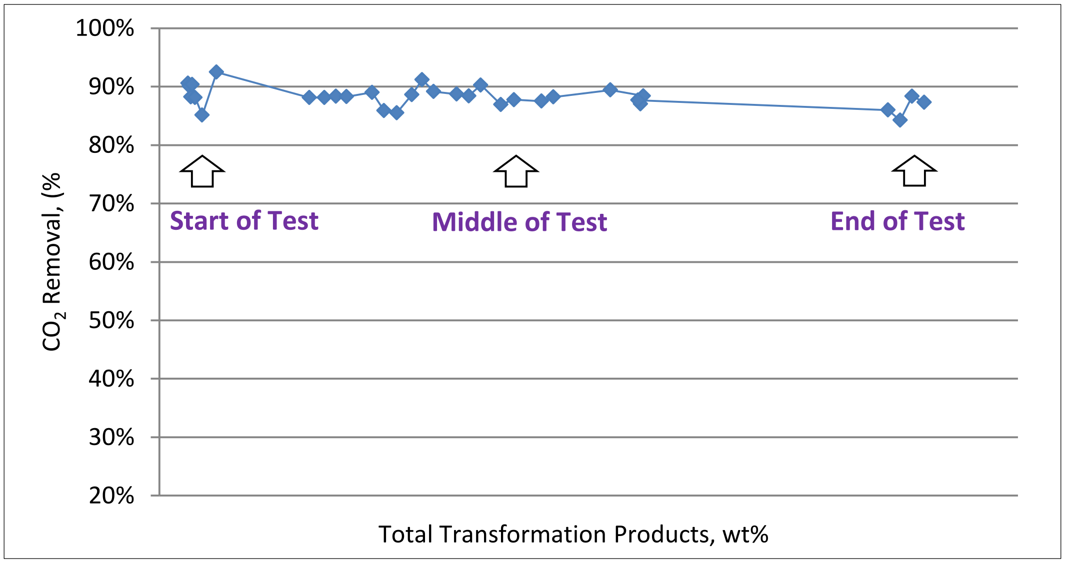


Figure 5. CO_2 Removal over Time for the Cansolv Solvent

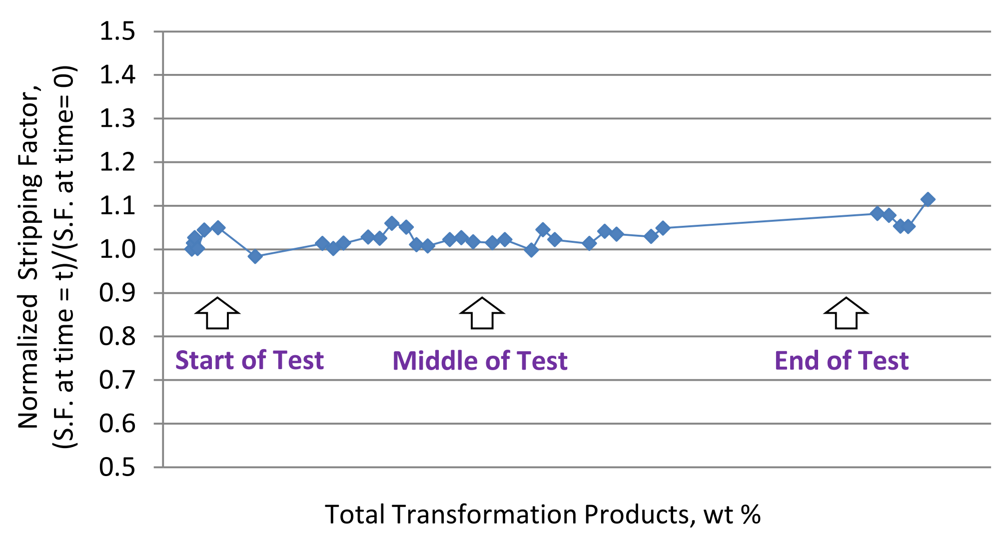


Figure 6. Normalized Stripping Factor over Time for the Cansolv Solvent

Similar behavior was observed for the stripping factor, as its performance did not worsen until the later portion of the piloting campaign, as demonstrated in Figure 6. It should be noted that the increase in stripping factor was marginal; the maximum observed was about 10 percent. For commercial applications, the total transformation product concentration will be controlled below the value measured near the halfway point of the test. A thermal reclaimer unit will be used to ensure process performance is not hindered. Also, it is important to note that the results shown for this test were generated in the absence of intercooling or any energy integration options.

Figure 7 plots lean solvent total alkaline concentration versus operational hours. The concentration was determined by titration; therefore, any degradation/transformation products which retain alkalinity were incorporated in the analysis. The results demonstrate that lean solvent total alkaline concentration was controlled near 50 wt%, even as some transformation products formed.

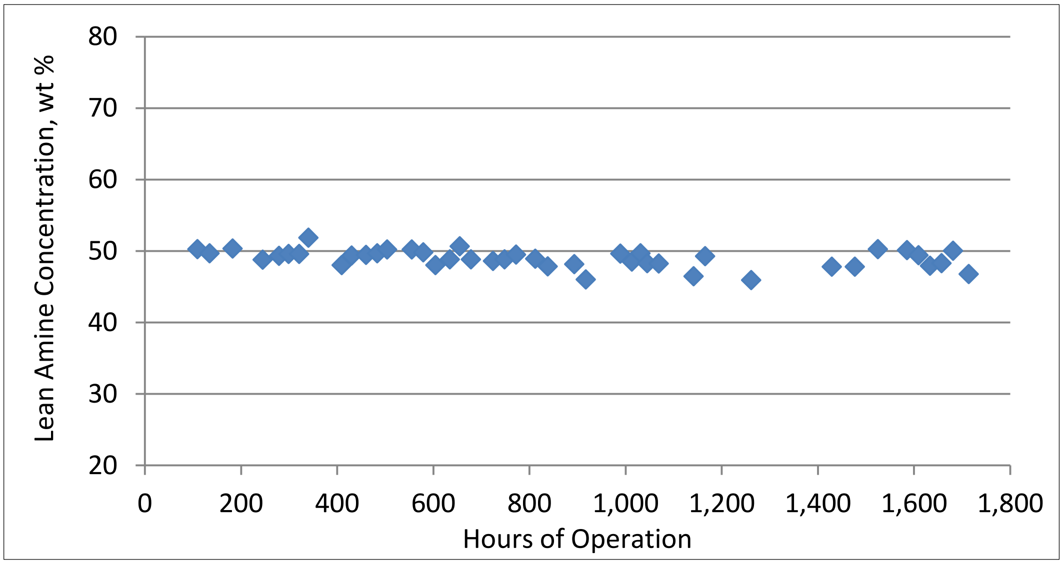


Figure 7. Lean Solvent Total Alkaline Concentration versus Operational Hours for the Cansolv Solvent

2.3.2 Gas Sampling

Gas sampling was performed using an impinger train developed at the NCCC, and the liquid collected was sent to Shell/Cansolv Laboratories for analysis of amine and degradation products. The sample system is shown in Figure 8. The gas is extracted isokinetically to obtain a representative gas sample. An ice bath removes both droplets and condensable liquids in an Environmental Protection Agency (EPA) Modified Method 5 (MM5) sample system. Contact between liquid and gas is minimized and gas is never bubbled through liquid. One of the impingers has an impaction plate to help collect small droplets. Downstream of the ice bath is a manifold section where smaller gas flows can be drawn through sample systems.

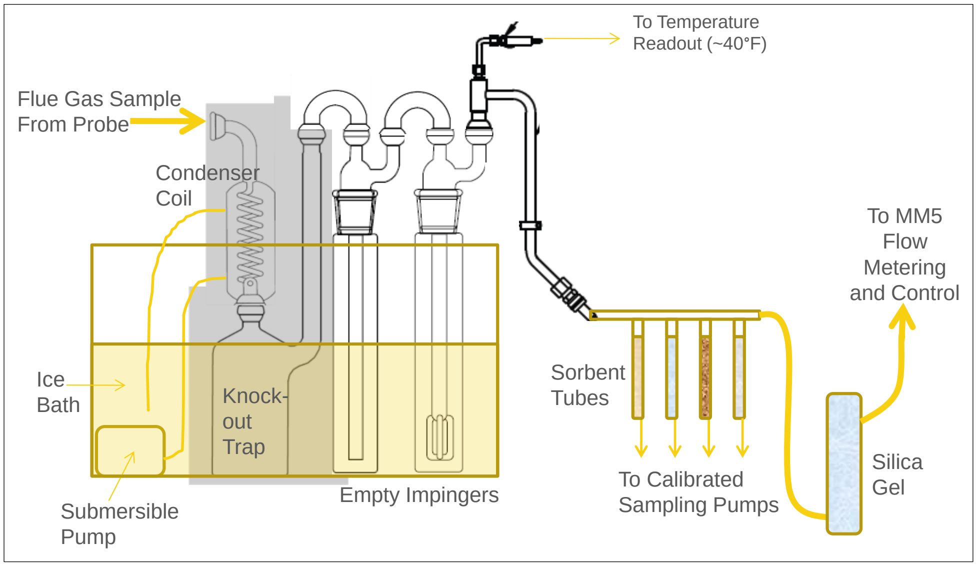


Figure 8. NCCC Gas Sampling Train Used to Measure Carryover of Degradation Products

Results of the amine emission surveys performed at NCCC have shown that amine emissions are considerably influenced by the composition of the flue gas—the more contaminated the flue gas entering the CO_2 capture system, the greater the resulting amine emissions will be. That is, the concentration of acid mist (sulfite), particulate, and other flue gas contaminants significantly affect amine emissions. To evaluate this phenomenon further, gas emissions tests were conducted with different quality flue gases. Three different flue gas streams were tested:

- Typical coal combustion flue gas
- Simulated natural gas flue gas
- Ambient air

A total of 14 gas sampling tests were performed, and the average results from these tests are summarized in Table 2. The results presented are valid only for the PC4 and cannot be applied to other pilot or commercial units since the concentration of acid mists and other contaminants such as particulates will vary and will influence amine emission results differently. Also, the results are valid only for the DC201 solvent; generally, different amines will exhibit different results due to dissimilarities in physical properties. The results demonstrated 33 and 77 times higher emissions compared to the air emission test for simulated natural gas (diluted coal gas) and standard coal flue gas, respectively.

Table 2. Amine Emission Results for Cansolv Solvent Testing

Gas Type	*Sulfite Content, ppmv*	*DC201 Emission Ratio to Air*
Air	0	1
Simulated NG Flue Gas	0.3	33
Typical Coal Combustion Flue Gas	1.3	77

Sampling was also performed on lean solvent over the course of the test campaign to analyze for metals and anions. Figure 9 provides the sampling results for species that accumulated in the solvent over time.

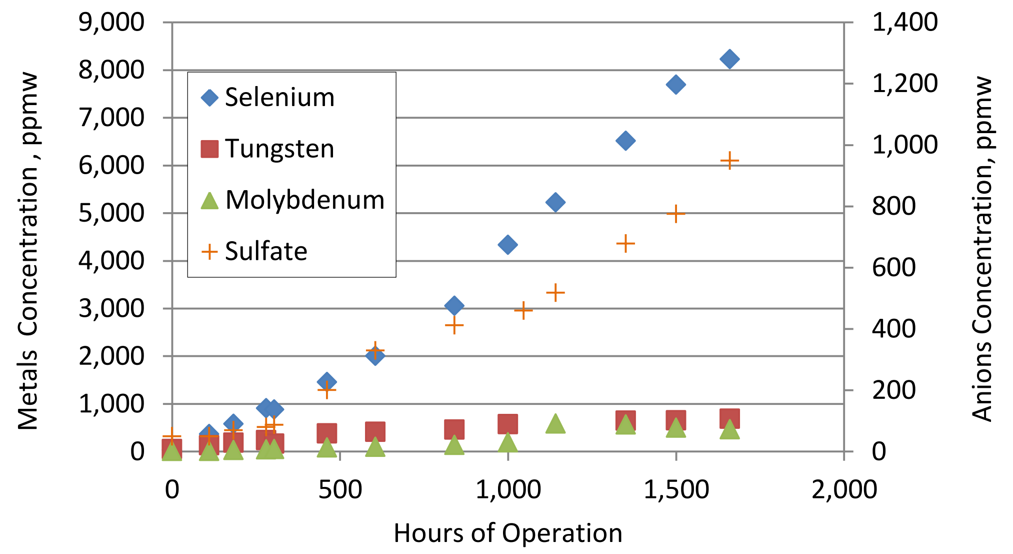


Figure 9. Concentration of Metals and Anions in Lean Cansolv Solvent over Time

Material coupons were installed for the test corrosion campaign for corrosion analysis. The results are pending as of this writing and will be reported once finalized.

2.3.3 Conclusions

Results of the Cansolv test campaign are as follows:

- Operated with the Cansolv DC201 solvent under simulated natural gas flue gas conditions for 1,715 hours
- Maintained process performance near 90 percent CO_2 removal for the duration of the testing
- Demonstrated a limited influence of transformation product concentration on CO_2 removal
- Demonstrated a maximum increase in overall energy consumption (stripping factor) of about 10 percent without intercooling or energy integration
- Completed solvent emissions testing showing 33 times greater emissions with natural gas simulated flue gas and 77 times greater emissions with typical coal flue gas over emissions with ambient air

2.4 MTR 1-ton/day CO_2 Capture Membrane Skid

In development of new membrane materials and processes, MTR has been testing its polymeric Polaris™ membrane for separating CO_2 from coal-derived flue gas. The membrane test skid includes two membrane module designs required for commercial units, cross-flow membrane (CFM) and countercurrent-swept membrane (CSM) modules. The skid processes 250,000 scf/day of flue gas drawn from downstream of the pre-scrubber, and is designed to capture one ton/day of CO_2 with a capture efficiency of 90 percent. Operational experience with the 1-ton/day system is being used to support a scaled-up membrane system to capture 20-ton/day of CO_2.

Figure 10 is a schematic of the skid. The incoming flue gas is cooled by chilled water, and the condensate is removed in the separator upstream of the flue gas compressor. The flue gas leaves the compressor at around 300°F and 45 psia before being cooled to around 100°F by chilled water. The condensate is removed in a separator, which also includes a coalescing filter, before the flue gas passes to the two first-stage membrane vessels. Each vessel contains two CFM membranes connected in series. Two second-stage membrane vessels each contain a single CSM membrane. The chilling circuits are not expected to be included in commercial designs and are used on the test skid to vary inlet flue gas conditions as part of parametric testing.

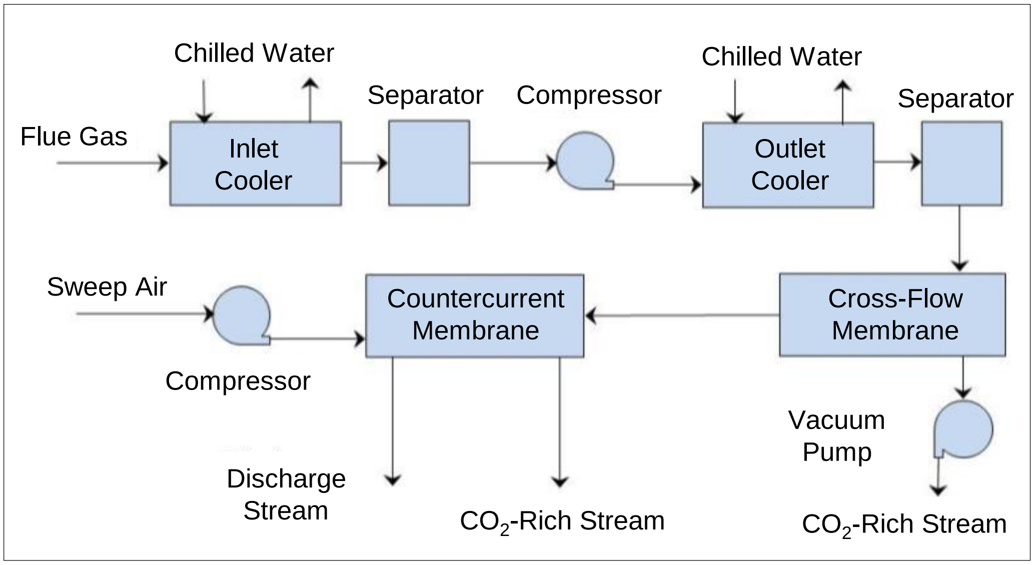


Figure 10. Schematic of MTR Flue Gas Membrane Skid

A vacuum pump on the permeate side of the first-stage membrane increases the pressure driving force to increase the amount of CO_2 removed to as high as 70 percent. The second-stage membrane extracts additional CO_2 from the residual flue gas by using sweep air on the permeate side to increase the concentration driving force. The additional removal is sufficient to increase the CO_2 capture efficient to 90 percent or higher.

Initial operation of the MTR 1-ton/day (TPD) unit began in December 2011 and has continued through 2013. Operation in 2013 utilized a new liquid ring flue gas compressor manufactured by NASH, which was installed in the last quarter of 2012. The compressor replacement was made to prevent corrosion problems encountered with the original compressor. In early 2013, several mechanical issues with the new compressor were resolved, annual service on vacuum pump and sweep air compressor was performed, and several new cross-flow and sweep air modules were installed.

The unit accumulated a total of 3,522 hours of operation in 2013. Of this, about 1,800 hours of operation were conducted with typical flue gas conditions while 1,300 hours were with diluted flue gas. The balance of operating hours were conducted using air when flue gas was not available and when purging was required. Overall performances are summarized below.

Figure 11 shows the cumulative performance of the modules tested with typical coal-fired flue gas in 2013, with respect to CO_2 removal and CO_2 enrichment in the permeate streams. Overall, these modules demonstrated stable performance at expected levels of separation, even after periods when the system was idle for repair/maintenance and PC4 outages. The fluctuation in module performance was largely due to variation in the ambient temperature.

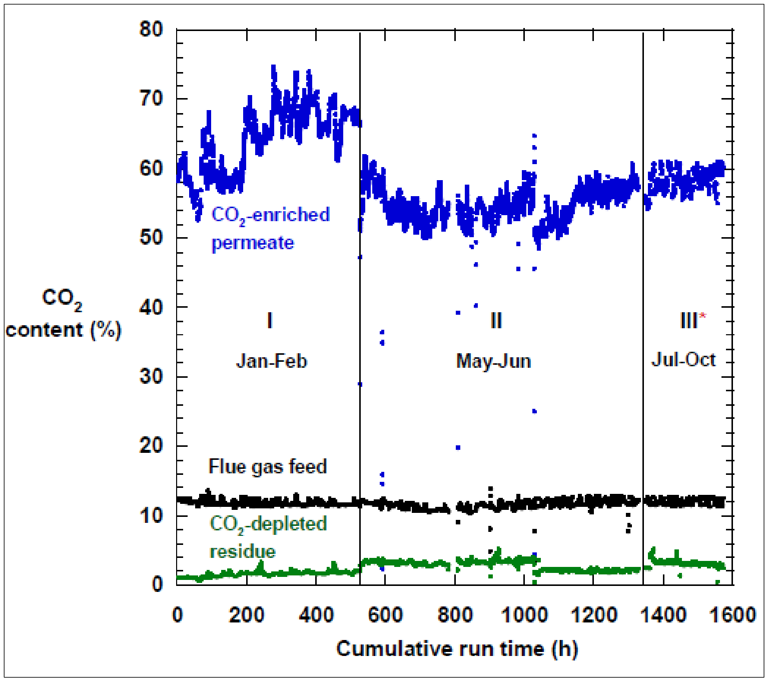


Figure 11. CO_2 Content of Inlet and Outlet Gas Streams of the MTR 1-TPD System during Operation with Typical Flue Gas

Figure 12 shows the temperature dependence of the CO_2 concentration in the permeate stream and of the CO_2 capture rate during typical flue gas operation. The data demonstrate consistent CO_2 capture of 90 percent at all temperatures in the range tested. The CO_2 capture rate increased with the temperature due to the corresponding increase in CO_2 permeance. However, CO_2 purity (CO_2 concentration in permeate stream) decreased with the temperature. This correlation can be used to predict the CO_2 enrichment by Polaris membranes at a given temperature.

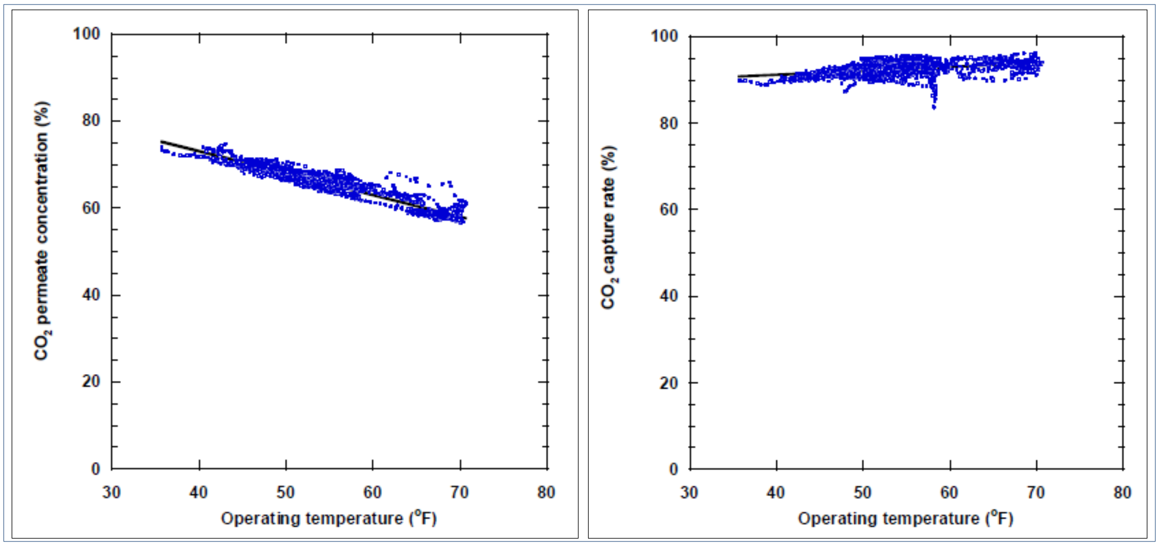


Figure 12. MTR Membrane Permeate Concentration and CO_2 Capture Rate as Functions of Temperature

Figure 13 provides a graph of the cumulative module performance with diluted flue gas. Diluting the flue gas with air reduced the CO_2 content of the inlet flue gas from 12 to 4 percent and resulted in a significantly lower CO_2 partial pressure in the feed gas. Separation of CO_2 by membrane technology is primarily driven by the differential in the CO_2 partial pressure. Therefore, without changing the feed gas flow rate and other operating conditions, less CO_2 (percentage-basis and mass-basis) was removed from the feed gas when air-diluted flue gas was used. Nevertheless, the system still achieved excellent performances with more than 80 percent CO_2 capture and an almost 8-fold CO_2 enrichment in the permeate stream.

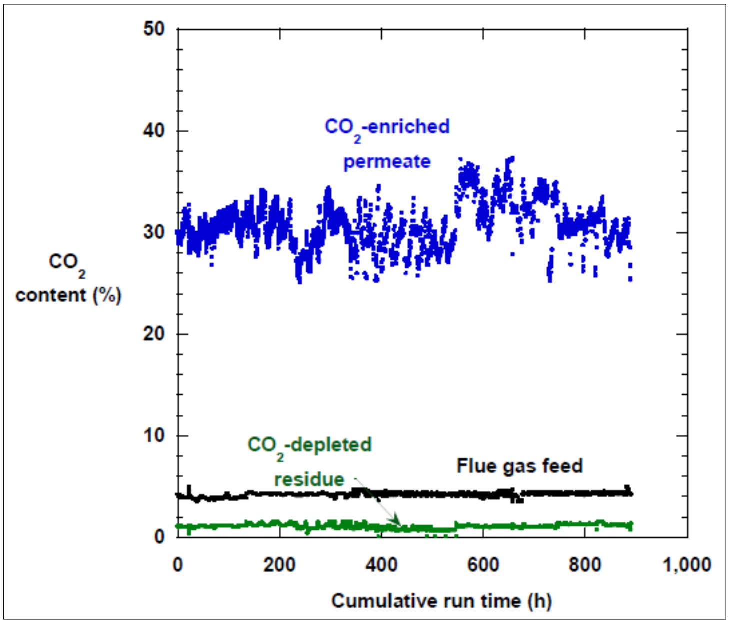


Figure 13. CO_2 Content of Inlet and Outlet Gas Streams of the MTR 1-TPD System during Operation with Diluted Flue Gas

MTR conducted a post-operation analysis of two cross-flow modules that were tested from December 2012 through July 2013. Table 3 shows the pure-gas performance of these modules after testing on the 1-TPD system relative to their original performance before the test. Both CO_2 permeance and CO_2/nitrogen selectivity remained almost unchanged (within the error range of the pure-gas module testing system), even after repeated system start-ups, shutdowns, and extended idle periods. MTR also found that fouling of membrane from condensation of water containing ammonium bisulfate can be avoided by purging the system with fresh air before shutting down the system. This finding specifically gained from this field testing is significant for extending the lifetime of the membrane in a commercial setting.

Table 3. Performance of Tested MTR Cross-Flow Modules Relative to Pre-Testing Performance

Module Number	*Normalized CO_2 Permeance*	*Normalized CO_2/N_2 Selectivity*
6704	87%	94%
6706	111%	130%

2.5 SRI International Sorbent

SRI International (SRII), through work funded by the DOE, is developing a novel carbon sorbent for CO_2 capture. 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 68 to 212^{o}F (20 to 100°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 176 to 212^{o}F (80 to 100°C)

Figure 14 provides micrographs of the sorbent.

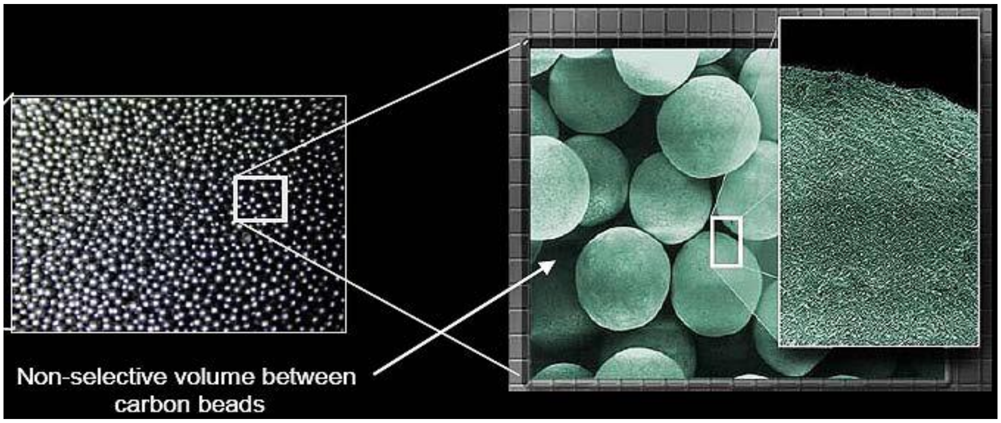


Figure 14. Micrographs of SRI International Sorbent

The SRII test unit 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 design was tested 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.

In 2013, SRII completed the sorbent test unit design and fabrication and had the skid delivered to the PC4 in October. Installation and two weeks of commissioning and operation with flue gas were also completed in October, after which SRII personnel incorporated minor design changes to improve operation. Testing of the sorbent unit will resume in the first quarter of 2014 for a planned duration of 1,000 hours. The installed unit is shown in Figure 15.

Figure 15. SRI International Sorbent Unit Installed at PC4

2.6 MTR 20-ton/day CO_2 Capture Membrane Skid

MTR is currently working to install a 1-MWe-scale, 20-ton/day CO_2 membrane test skid based on the 1-ton/day CO_2 system test results. The overall project objectives for this DOE-funded project:

- Optimize membrane performance, module pressure drop, and module fouling resistance
- Conduct a six-month field test of the 1 MWe membrane system
- Analyze the performance of the membrane system, determine how it would be best integrated with an electric power plant, and prepare a comparative study of the membrane-based CO_2 capture process versus other capture technologies

- Determine the impact of recycle air on boiler performance
- Evaluate the membrane potential in an industrial application

MTR completed the 20-TDP unit design in early 2013 and completed a design hazard review. MTR ordered all the major components, and skid construction and assembly were underway. Delivery of the system is expected in April and commissioning in May 2014, with testing to begin shortly thereafter.

The NCCC completed engineering, procurement, and construction for the 24-inch thick concrete containment and foundation slab (shown in Figure 16) and for concrete blocks onto which MTR equipment skids are to be placed. Additional space was also allocated for MTR's future new plate-and-frame sweep air module adjacent to the 20-TDP skid. Installation of the cooling water supply and return tie-ins for the project was completed. A motor control center was purchased in December, and delivery is expected in early February 2014.

Figure 16. Pilot Bay 3 Foundation to Support MTR 20-TPD Unit

2.7 Linde-BASF Solvent and Process

Linde and BASF will operate 1-MWe CO_2 capture pilot plant processing up to 30 tons CO_2 /day at the PC4 beginning in 2014. The technology, depicted in Figure 17, incorporates BASF's novel amine-based process along with Linde's process and engineering innovations. The group plans to implement parametric tests to achieve target performance as well as long duration tests to demonstrate solvent stability and obtain critical data for scale-up and commercial application.

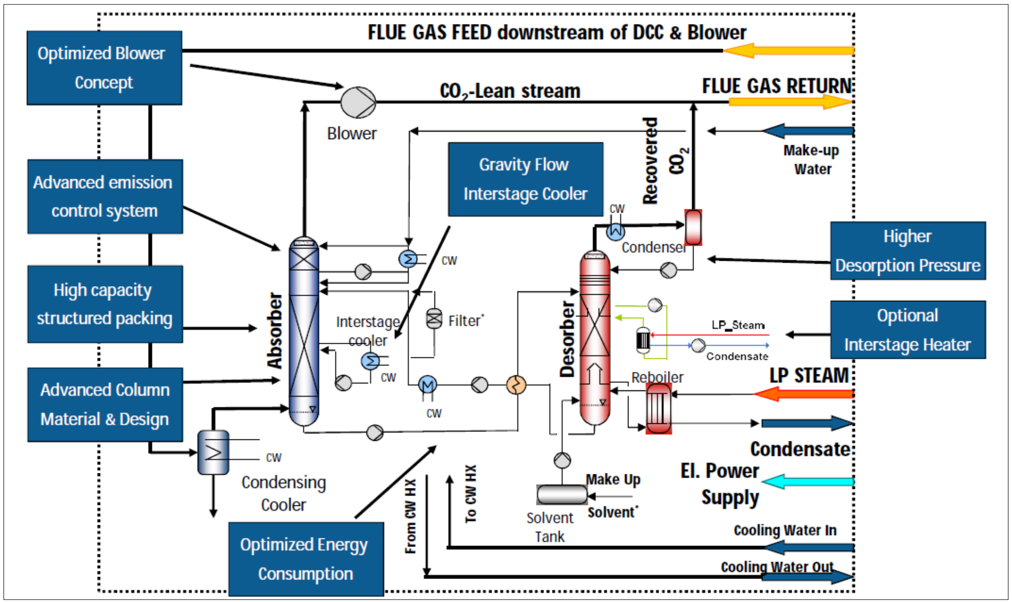


Figure 17. Linde-BASF Process Diagram

Linde-BASF completed detailed design and equipment procurement and initiated shop fabrication of the major components, such as absorber and stripper columns, structural steel, and an analyzer building. Fabrication of the process modules was completed by the end of the year. The NCCC finalized site preparations, including a foundation and sump system, and installed utility tie-ins and solvent handling and storage systems. Figure 18 provides a photograph of the module fabrication and a 3-D model of the Linde-BASF process installed adjacent to the PSTU. Mechanical completion is expected in May 2014 with commissioning activities beginning soon thereafter. Testing is planned to continue into 2015.

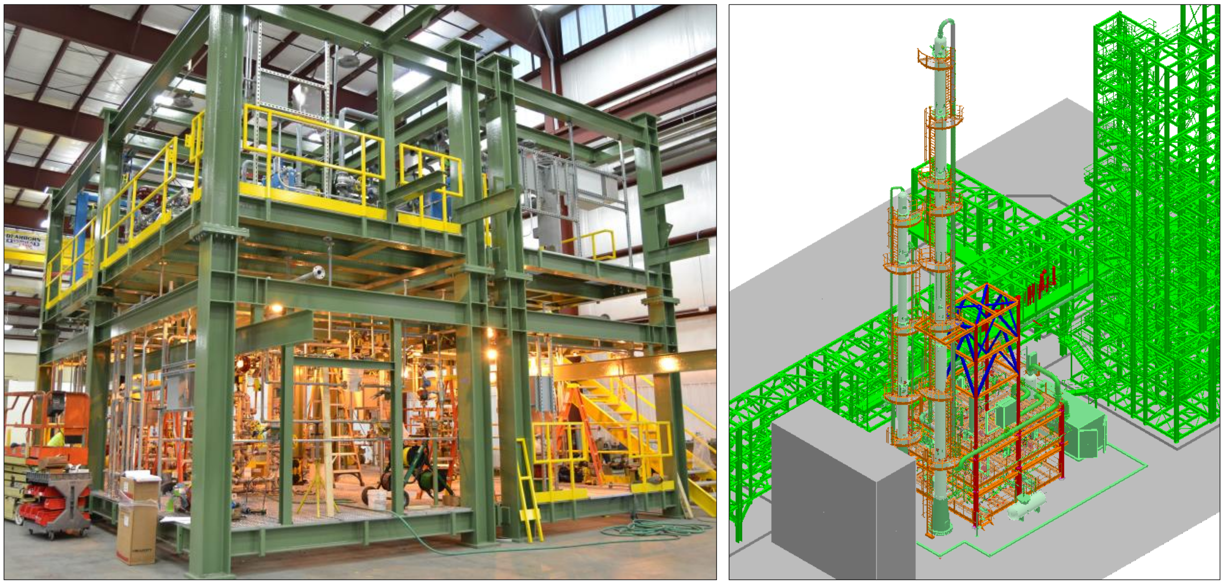

Process Module Fabrication
Model View of Installed Pilot Plant

Figure 18. Equipment Fabrication and 3-D Model of Linde-BASF Process

2.8 Additional Testing Planned for 2014

In addition to test plans for post-combustion CO_2 capture technologies mentioned in the preceding sections, PC4 operations in 2014 will include:

- Carbon Clean Solutions' solvent in the PSTU
- The DOE's C2U bench-scale sorbent unit
- Carbon Capture Scientific's solvent system

2.9 PC4 Modifications

2.9.1 Balance of Plant Upgrades

To accommodate simultaneous testing of pilot-scale units with excess flue gas for testing in the bench-scale area, several upgrades to BOP equipment were underway. The total capacity of the PC4 will be about 30,000 lb/hr upon completion of the modifications, which include:

- A forced draft blower delivering 20,000 lb/hr with a higher delivery head replaced the original blower with a delivery rate of 12,000 lb/hr.
- The random packing in the pre-scrubber was replaced with structured packing to maintain high SO_2 collection efficiency at the higher flue gas flow rate. Due to the capacity limit of the pre-scrubber demister, the maximum throughput of the pre-scrubber with the structured packing is 17,000 lb/hr.
- To meet the higher cooling duty requirements, a second cooling tower cell was added along with larger water circulation pumps.
- New electrical infrastructure was installed, which included a 2,500 KVA transformer and switchgear. Final tie-ins are planned for 2014.
- The original blower will be relocated to the pilot-scale test area, and a new pre-scrubber and associated equipment will be installed in 2014.

2.9.2 Slipstream Solvent Test Unit

The NCCC is adding the SSTU to increase the flexibility of the PC4 by allowing testing of solvents (such as those in early stages of development) available only in amounts smaller than the 4,000 gallons required for the PSTU. The SSTU comprises a pre-scrubber, condenser, absorber, regenerator, and associated equipment along with analytical instrumentation. During the year, NCCC engineers finalized the design of system modifications and additional equipment, layout, and utility connections. The SSTU module and its absorber, regenerator, and pre-scrubber were installed, utility tie-ins were completed, and procurement was underway for the new equipment needed such as a wash tower, flash tank, and solution filter bank.

2.10 Engineering Studies

The NCCC's Engineering and Economic Evaluations group completed a Post-Combustion CO_2 Capture (PCC) baseline study and sent a draft report to NETL. The following cases were included in the study:

- Pulverized Coal (PC) plant without CO_2 capture
- PC with 90 percent CO_2 capture using MEA
- PC with 50 percent CO_2 capture using MEA

An investigation of the effects on the steam cycle of turning off one of two 50 percent MEA CO_2 capture trains was also completed.

The NCCC used models in AspenPlus, CHEMCAD, and Thermoflex to calculate heat and material balances for this supercritical greenfield plant. Proprietary Southern Company costs for capital and operations and maintenance were used along with an MEA system capital cost estimate from Worley Parsons. Emissions and water-use calculations were also completed.

A study of a PC plus PCC plant using spiral-wound membranes was begun after collaboration with NETL and the Electric Power Research Institute on the study plan. Separate heat and material balances for the PC plant and for the CO_2 capture system were completed using CHEMCAD and Thermoflex. The NCCC group worked with ChemStations and DOE to have a unit operations block for membranes developed for CHEMCAD. This was tested, modified, and validated, and will soon be available to the public in the next release of CHEMCAD.

Another study for the evaluation of a PC plant with advanced solvents for post-combustion CO_2 capture was begun after a similar collaboration on the study plan. This study is building on the baseline post-combustion capture study to evaluate advanced solvents that have been tested at PC4. Permissions were received from solvent vendors to use their process data in this study. Test data from PC4 operations were screened, evaluated, validated against data from other sources, and checked for internal consistency. Major equipment sizing began for one solvent. Calculations were completed to determine the overall effect on the steam cycle of different extraction steam pressures. Development of spreadsheet templates began for estimating the capital and O&M costs.

Non-proprietary typical boiler air-side info was sent to NETL for possible use in their Quality Guidelines for Energy System Studies.

3.0 GASIFICATION

The NCCC gasification process, represented in Figure 19, 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 (PCD); and continuous ash depressurization systems for ash cooling and removal.

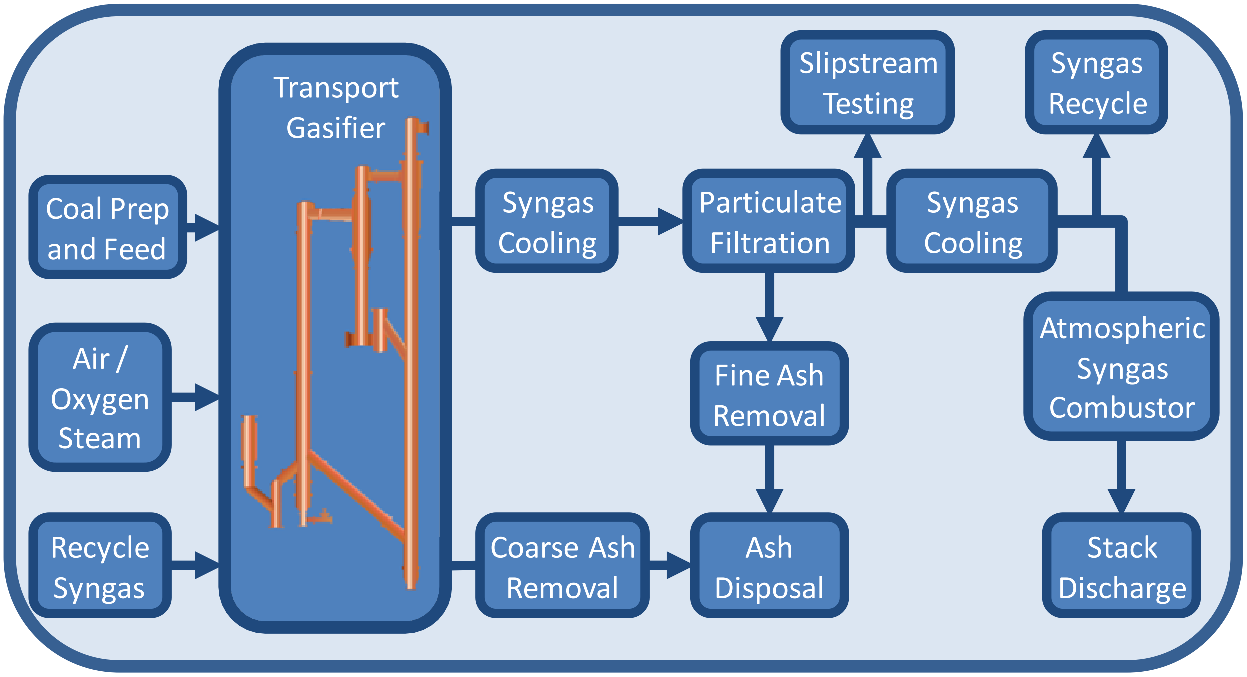


Figure 19. NCCC Gasification Process

During the year, the gasification process operated over three test runs, R10, R11, and R12, for a total of more than 2,000 hours. The feedstock for runs R10 and R12 was Powder River Basin (PRB) coal, and for R11, Mississippi lignite from the Liberty Fuels mine in Kemper County was used. At the conclusion of R12, the gasification process had operated for over 20,000 hours. Figure 20 presents the accumulated on-coal operation of the process, including initial operation in combustion mode.

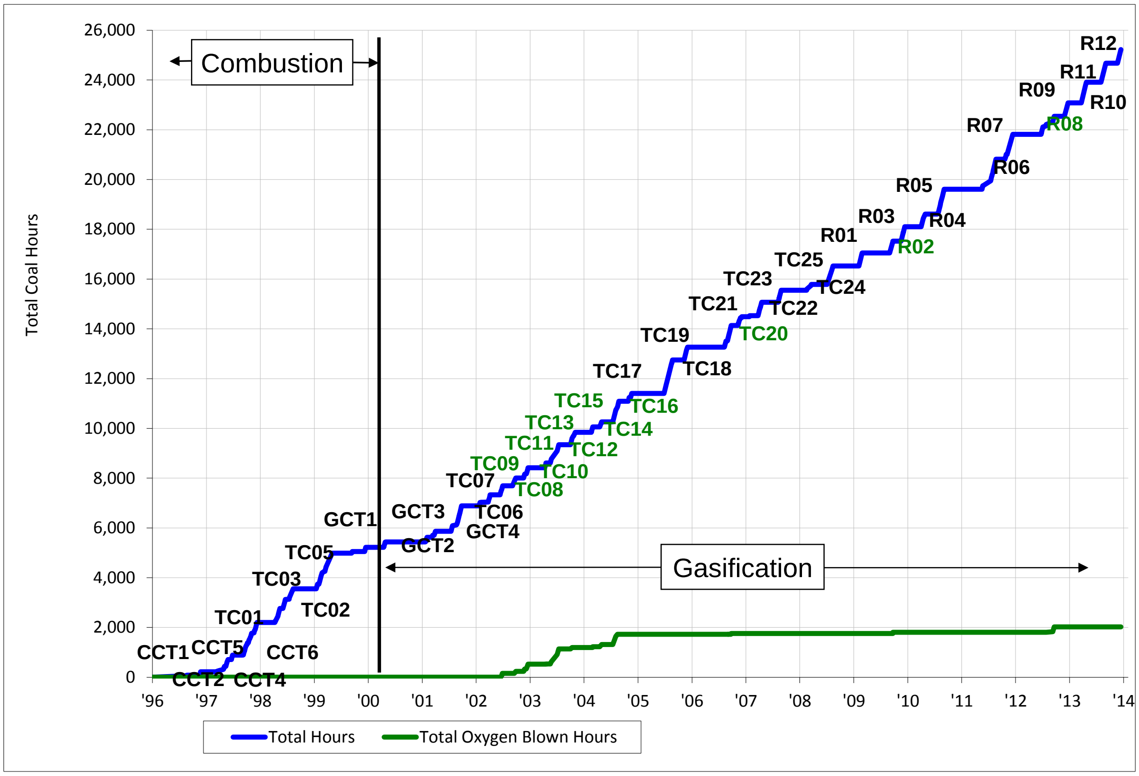


Figure 20. Historical Operation of the NCCC Transport Reactor/Gasifier

3.1 Gasification Operation

Gasifier operation was stable during runs R10, R11, and R12, with steady-state carbon conversions comparable to previous test runs, as demonstrated by Table 4. All data points for historical carbon conversion were collected from runs using the current gasifier configuration, in use since 2006. The historical lignite data was taken from runs using Mississippi lignite from the Red Hills mine, which is close in proximity to the Liberty Fuels mine and has lignite similar in fuel properties.

Table 4. Steady State Carbon Conversions for 2013 Gasification Runs and Historical Operation

	Maximum	*Minimum*	*Average*
R10 Carbon Conversion, %	99.9	98.9	98.9
R12 Carbon Conversion, %	99.9	98.4	98.8
Historical PRB Coal Carbon Conversion, %	99.6	95.3	98.4
R11 Carbon Conversion, %	99.9	98.2	98.6
Historical Lignite Coal Carbon Conversion, %	99.9	94.6	98.1

Previous modifications to the automatic temperature control scheme, which adjusts the air flow based on gasifier outlet temperature, have been effective in controlling the temperature to within 5F^{o}. In R11, changes in gasifier operating characteristics with the Mississippi lignite as opposed to PRB resulted in larger temperature fluctuations and necessitated additional modifications to the control scheme. Therefore, the gasifier temperature set point was raised, the individual and total air flow controllers were tuned, and the air flow split to the lower and upper mixing zones was modified. Figure 21 charts the gasifier outlet temperature before and after implementation of the changes and demonstrates the improvement achieved.

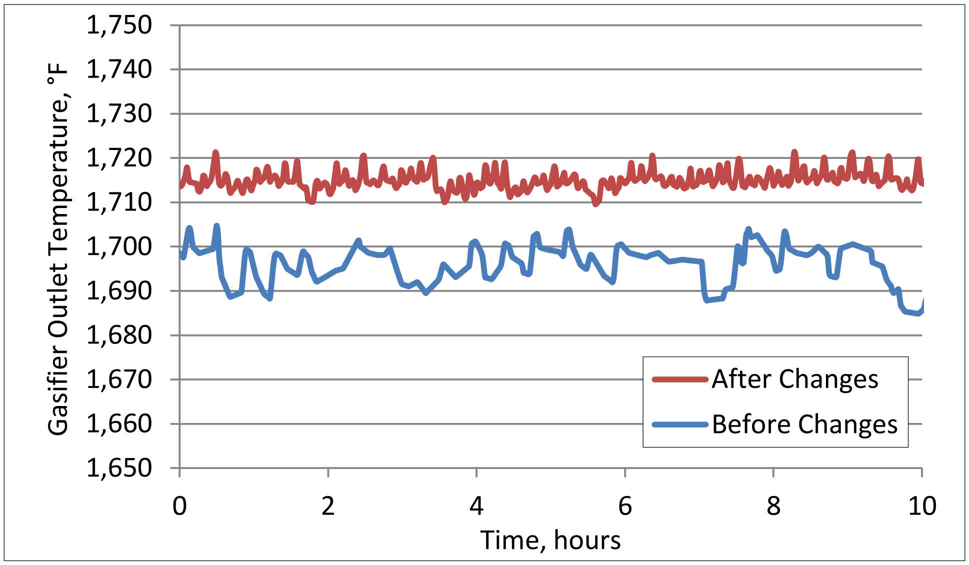


Figure 21. Gasifier Outlet Temperature before and after Changes Made to Control Scheme

3.2 Sensor Development

3.2.1 Sapphire Thermowell for Gasifier Service

Previous testing of Emerson’s Rosemount sapphire thermowell showed excellent responsiveness to temperature changes, but the temperature measurement drifted over time. Over more than 2,700 hours of operation, the thermocouple housed in the sapphire thermowell showed a measurement drift of more than 10 percent compared to a reference thermocouple with an HR-160 thermowell. Vendor inspections indicated that the drift was due to damage during shipment.

To prevent damage to the thermowell, Emerson and NCCC staff collaborated on different designs for mounting the thermowell in the gasifier. During R11, a new mounting technique was utilized, which appeared to improve operation with the sapphire thermowell. As the graph in Figure 22 indicates, the thermocouple with the sapphire thermowell read slightly lower than the reference thermocouple as it had previously, but the difference was consistent and averaged less than one percent. The Rosemount system responded to gasifier changes well, while maintaining mechanical integrity. The thermowell was returned to Emerson for inspection, and further long-term testing is planned.

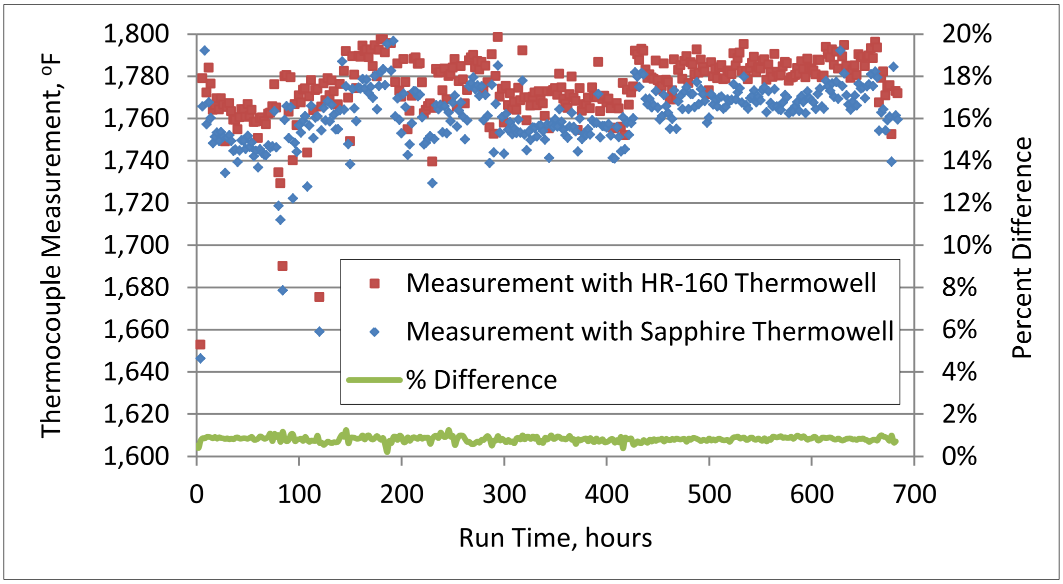


Figure 22. Comparison of Thermocouple Measurements Using Sapphire and HR-160 Thermowells

3.2.2 Coal Feeder Instrumentation

Measurements with the DensFlow coal flow meter continued to show disagreement in coal feed rates from the weigh cell calculation. Collaboration with the flow meter supplier is ongoing to improve the flow meter performance.

The solids level probes used in operation of the developmental Pressure Decoupled Advanced Coal feeder continued to perform reliably. The Dynatrol vibration level probes have accumulated 7,685 hours of operation, and the Drexelbrook point sensitive probe has accumulated 6,485 hours of operation.

3.3 Hot Gas Filtration

The PCD operated with excellent filtration performance during the 2013 runs, with particulate outlet loading consistently below the sampling detection limit, which is 0.1 part per million by weight (ppmw). Research efforts continued on the long-term evaluation of filter material performance. The filter elements installed consist of sintered fiber elements—elements manufactured by Porvair and HR-160 elements from Pall—and sintered powder filter elements—Iron Aluminide (FEAL) elements from Pall and elements with a high-alloy material from Mott. Figure 23 displays the results of cold flow pressure drop measurements taken for elements removed from the PCD and cleaned for inspection. As indicated in the figure, the FEAL elements have been tested for the longest continuous exposure time, some having accumulated over 16,000 hours of gasification service.

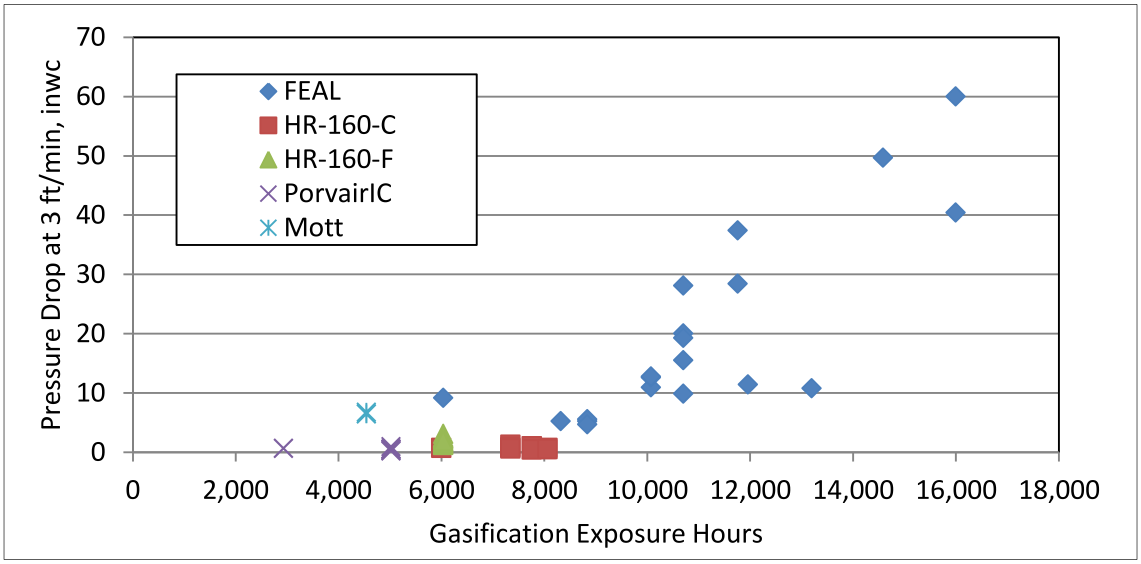


Figure 23. Cold Flow Pressure Drop Measurements for Hot Gas Filter Elements after R12

After 16,000 hours of operation (corresponding in time to about two years of operation in a commercial plant), the FEAL elements have consistently demonstrated extremely high filtration efficiency despite the corrosion presumably causing increasing pressure drop, and are considered suitable for commercial applications. The corrosion rate for these elements is expected to be considerably lower in a commercial unit, which would not have as much thermal cycling (compared to a research facility) at conditions promoting degradation of the protective alumina layer. Due to high baseline pressure drop, the oldest of the FEAL elements were removed from service following run R12, and they were replaced with newer FEAL elements for further testing of this material.

Two filter element test partners, Mott Corporation and Bekaert, continued to evaluate materials for filter element development with coupons placed in the PCD downstream of the filter elements. Mott originally installed 65 coupons in May 2007 made of 16 different alloys including two types of Inconel, four Hastelloy materials, three of Iron Aluminide, three of 310 stainless steel, one Silcolloy coated material, and three experimental alloys. Bekaert's coupons were initially installed in July 2010, and these consist of five coupons using Fecralloy, Inconel, Hastelloy, Nicrofer, and an experimental alloy. All these coupons were left installed following R12 for additional syngas exposure in future runs.

3.4 Water-Gas Shift and COS Hydrolysis Catalysts

Water gas shift catalyst evaluation is completed in one of three pressure vessels shown in Figure 24. The vessels and the lines delivering the syngas are heavily trace heated and insulated to maintain the required operating temperatures. Some of the key design parameters for the vessels are presented in Table 5.

Figure 24. SCU Reactor Vessels Used for WGS Catalyst Evaluation

Table 5. Design Parameters for WGS Catalyst Reactor Vessels

Design Parameter	***Value***
Vessel Material of Construction	310 Stainless Steel
Design Pressure, psia	365
Design Temperature, ^{o}F	1,000
Height of Parallel Section, inches	48
Internal Diameter, inches	5.2

The syngas at the inlet of the PCD of the gasification process is analyzed using two on-line gas chromatographs and a Non-Dispersive Infrared CO/CO_2 meter, and this information is used as the inlet syngas composition to the WGS vessel. The syngas composition leaving the WGS vessel is provided by gas chromatographs. Syngas moisture content is determined by condensation measurement, as this has proved to be more accurate than using continuous analyzers. The vessel is equipped with an inlet flow meters and flow control valves for syngas and for steam. The meters are configured so that they can be checked with a known flow of nitrogen prior to start-up and at intervals during the run.

An undisclosed WGS catalyst supplier began testing a catalyst under development in 2011 using coal-derived syngas. Operation with the WGS catalyst has included parametric studies and long-term material evaluation. Through the end of 2013, the testing had encompassed more than 3,500 hours of syngas operation, with no significant degradation of the catalyst. Operation was typically conducted at a syngas flow rate of 50 lb/hr, a temperature of 480^{o}F, a pressure of 180 psig, and a steam-to-CO ratio of 1.0 (using only the steam inherent in the syngas). Figure 25 plots the CO conversion achieved for all testing from 2011 through 2013. The steam-to-CO ratio was much higher with Mississippi lignite due to the relatively higher coal moisture, and the CO conversion was correspondingly greater.

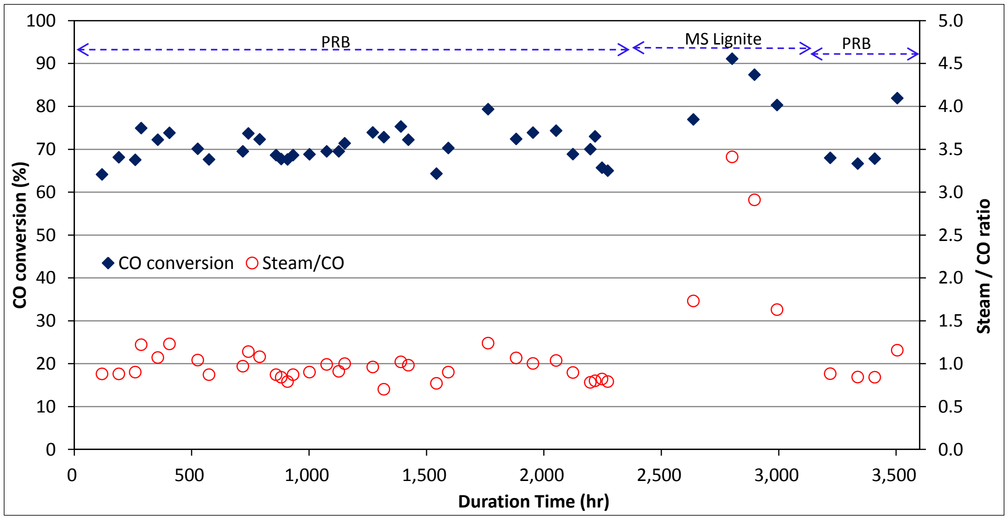


Figure 25. CO Conversion and Steam-to-CO Ratio for WGS Catalyst Testing from 2011 to 2013

Figure 26 provides the results of parametric testing of the WGS catalyst with syngas produced from PRB coal and lignite. In the range tested, the temperature did not significantly affect CO conversion. Lower space velocity achieved by reducing the syngas flow rate to 25 lb/hr increased the conversion to slightly above the estimated equilibrium value.

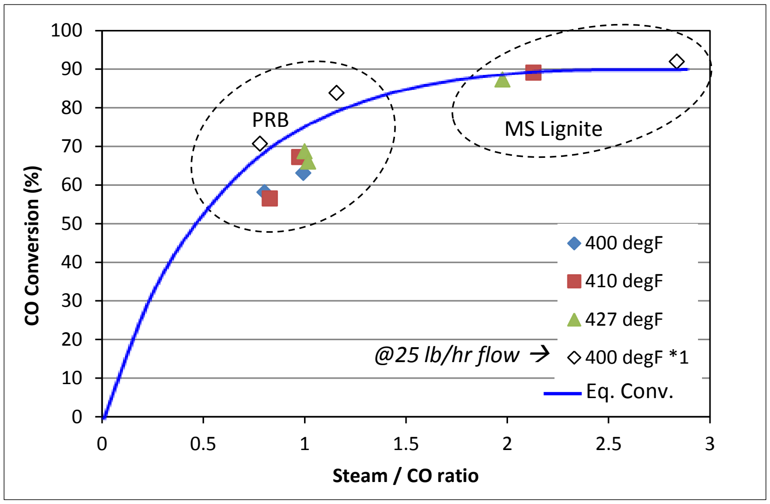


Figure 26. CO Conversion of WGS Catalyst during Parametric Testing

The same catalyst developer also provided a COS hydrolysis catalyst made with a honeycomb configuration, which was tested in R12 for about 400 hours. Further testing is planned for 2014 of both the WGS and COS hydrolysis catalysts.

3.5 Johnson Matthey Mercury Sorbent

In collaboration with the NETL, Johnson Matthey has been developing a palladium-based sorbent to remove mercury and other trace contaminants, such as arsenic and selenium, at high temperature in coal gasification processes. Compared to low-temperature capture by activated carbon, high-temperature capture of these trace elements retains the high thermal efficiency of coal gasification power generation.

Testing at the NCCC has been on-going since 2008, with the most recent testing conducted during run R10, making a total of more than 3,200 hours. The sorbent has demonstrated greater than 99 percent capture of mercury, arsenic, and selenium. To optimize the sorbent, palladium loadings of 2 wt% and 5 wt% have been tested for performance comparisons.

For the R10 run, the NCCC installed a new reactor for continuous sorbent evaluation at a syngas flow rate of 50 lb/hr, and the mercury sorbent with 2 wt% palladium was tested for 490 hours at 400°F. The NCCC took four sets of syngas samples using the EPA Method 29 impinger train to determine the inlet concentration of mercury, selenium, and arsenic and to detect any breakthrough of these metals in the outlet syngas. The samples were sent to an external laboratory for analysis, and the results are presented in Table 6. No breakthrough was detected, so only the inlet concentrations are given.

Table 6. Metals Concentrations during Mercury Sorbent Test

Date	*Mercury*		*Arsenic*		*Selenium*	
	μg	*μg/Nm³*	*μg*	*μg/Nm³*	*μg*	*μg/Nm³*
4/9/2013	10.7	5.0	1.5	0.69	53.8	24.9
4/16/2013	13.6	6.3	1.1	0.51	27.0	12.5
4/18/2013	12.4	5.7	1.4	0.65	58.5	27.1
4/22/2013	11.9	5.5	1.2	0.55	32.0	14.8

Near the end of the run, NCCC used GC analysis on the exit gas stream to determine if the catalyst was promoting the water-gas shift reaction; no water-gas shift activity was detected. Following the run, the sorbent was removed and returned to Johnson Matthey for analysis.

As the heating on the newly installed reactor was not able to attain the desired 450°F operating temperature, additional heating capacity using mineral-insulate cable was supplied following the run. The reactor was also modified so that the sorbent can be installed with mesh at 2-inch intervals, allowing the sorbent to be removed in discrete layers following operation and the absorption profile to be determined. Further testing of the Johnson Matthey sorbent is planned for 2014.

3.6 Ohio State University Syngas Chemical Looping

Ohio State University has developed the SCL process to convert syngas into separated hydrogen and CO_2 streams using a countercurrent moving-bed reducer/oxidizer reactor system. The project is funded by DOE's Advanced Research Projects Agency-Energy, which is providing OSU $5 million for this project. SCL has been successfully demonstrated at bench and sub-pilot scales, and will be tested at the NCCC at a 250-kW pilot scale utilizing up to 900 lb/hr of syngas.

Following NCCC's installation of the foundation micropiles, OSU's construction team installed the foundation, structure, and process components adjacent to the NCCC gasification structure, as show in Figure 27. The NCCC installed an air compressor and syngas and utility connections and assisted in design and operations issues. Initial commissioning activities were completed on the SCL subsystems, and testing of the process with syngas is planned for run R13.

Figure 27. OSU Syngas Chemical Looping Process Structure

3.7 Additional Testing Planned for 2014

Gasification testing in 2014 will include continuation of previously mentioned technologies and others, including Southern Research Institute's Fischer-Tropsch catalyst and Stanford University's Tunable Diode Laser with added analyte capacity.

3.8 Gasification Process Modifications

Several modifications were made to the gasification process during the year to address equipment-related issues. These changes included installation of a new pressure letdown device for the Continuous Fine Ash Depressurization system to decrease construction costs of the system, and adding piping for fluidization inside the cooler of the Continuous Coarse Ash Depressurization system. Design work was ongoing for the replacement of the primary syngas heater and modifications to the PCD vessel.

4.0 PRE-COMBUSTION CO_2 CAPTURE

The SCU infrastructure for pre-combustion CO_2 capture testing provides for a wide range of test conditions. Figure 28 is a flow diagram of the SCU, which consists of small reactor vessels, arranged to allow operation in series or in parallel, and accommodates a range of flow rates, temperatures, and pressures. During 2013, several upgrades to the SCU were incorporated, and various tests with gas separation membranes, a CO_2 capture sorbent, and CO_2 solvents commenced.

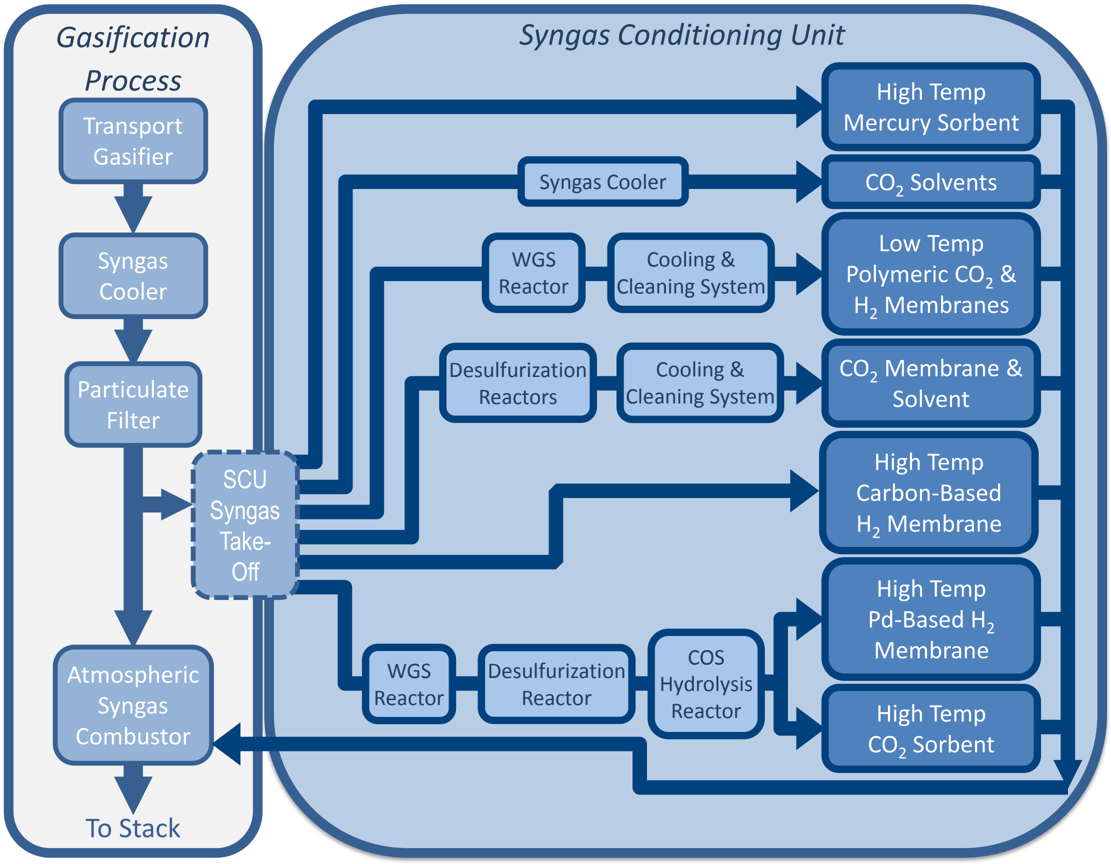
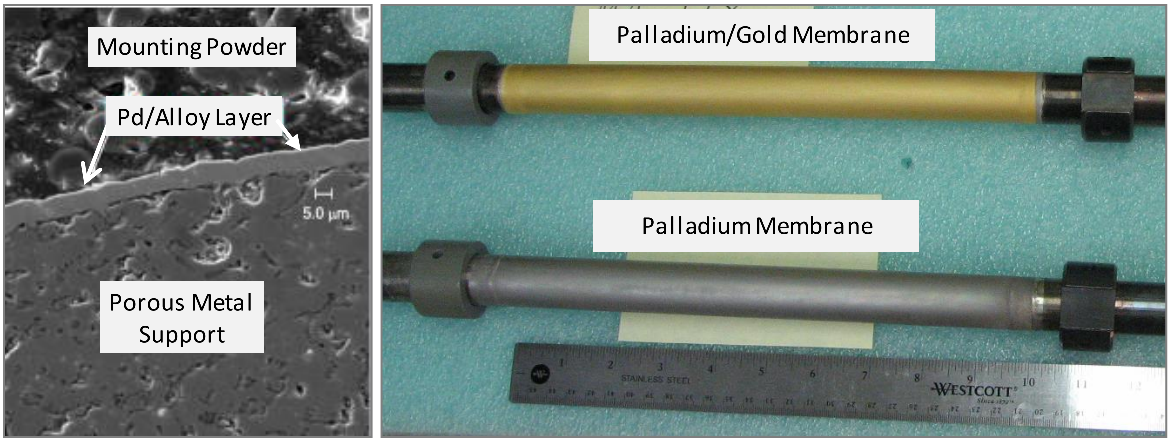


Figure 28. Syngas Conditioning Unit

4.1 Worcester Polytechnic Institute Membranes

WPI received a DOE award in 2010 to develop high temperature palladium-based membrane technology to separate hydrogen from coal-derived syngas. WPI's composite membrane consists of porous metal substrate (e.g. Inconel or stainless steel) onto which 7 to 12 microns thick dense hydrogen selective palladium (and other alloys) layers are deposited. Figure 29 shows the cross section of membrane layers and completed membrane tubes with various alloys.

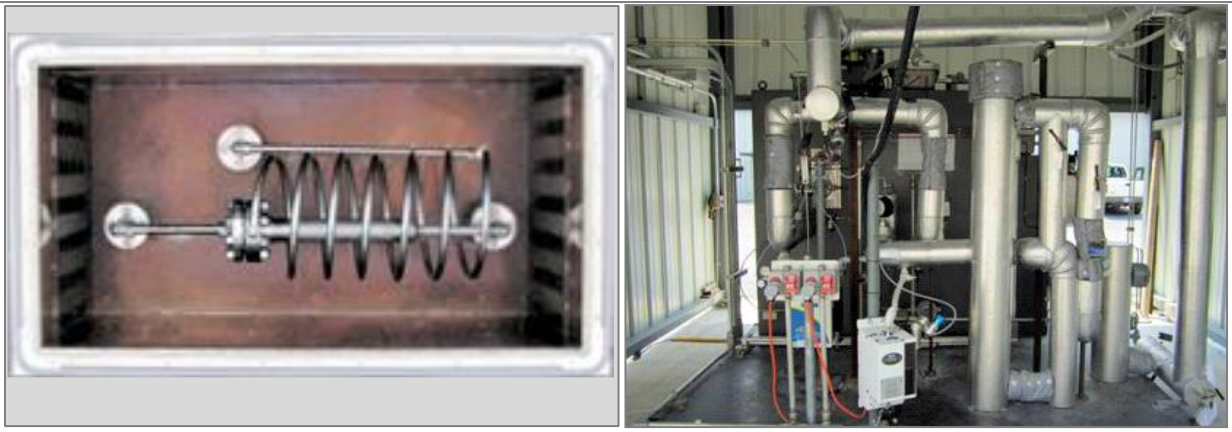


Composite Layers

Palladium Membranes on Metal Supports

Figure 29. WPI Hydrogen Membranes

Figure 30 shows the installed membrane test skid, including an oven, membrane module housing the membrane tube, sulfur guard bed, and ballast vessel. The membrane module was designed to process 10 lb/hr of syngas with hydrogen augmentation from gas cylinders to achieve hydrogen concentrations of 35 to 40 vol%.



Membrane Installed in Oven

Skid Piping and Equipment

Figure 30. WPI Membrane Oven and Skid

WPI's testing at the NCCC began in 2011, and has continued through the present time. As summarized in Table 7, WPI tested five membranes with various palladium and palladium/alloy compositions in 2013 for a total of 1,331 hours. The hydrogen produced during testing was typically above 99.5 percent in purity, except for two periods of testing (one with the palladium membrane in R10, and the other with a palladium/platinum membrane in R12) when leaks occurred.

Table 7. Membrane Testing by WPI in 2013

Test Run	*Membrane Composition*	*Operation Hours*
R10	Palladium	233
R10	Palladium/Gold	253
R11	Palladium/Gold	355
R12	Palladium/Platinum	336
R12	Palladium/Platinum	154

To verify its laboratory results showing higher resistance to sulfur poisoning with the palladium/gold alloy, WPI conducted testing during the R10 run with this alloy adding controlled amounts of hydrogen sulfide (H_2S). To regulate the H_2S syngas concentrations, sulfur species in the raw, shifted syngas were first removed by a zinc oxide sorbent upstream of the membrane. H_2S from gas cylinders containing 1,600 ppmv H_2S in nitrogen was added to the syngas via a new gas supply line installed by the NCCC. The H_2S-spiked syngas was then fed to the membrane module, bypassing the sulfur polishing bed on the WPI test skid.

The bottled H_2S was added to syngas at increments of 0.2, 0.3, and 0.5 slpm, corresponding to 3.7, 5.0 and 9.4 ppmv H_2S concentration in the membrane feed gas. Data showed that hydrogen permeance was reduced by 40, 48, and 60 percent at these respective H_2S concentrations. However, after the H_2S addition was stopped, the membrane permeance was fully recovered within 30 minutes. A repeated test confirmed the initial results. The remarkably quick recovery of hydrogen permeance following H_2S exposure and poisoning had not been reported before.

WPI will continue testing the palladium-based membranes in 2014, and has been working on a Phase II scale-up of the membrane technology. The initial scale-up module will contain multi-tube membranes using the current syngas flow capacity of 10 lb/hr. Performances from testing of this intermediate module will guide the planned 50-lb/hr scale-up module design.

4.2 Membrane Technology & Research Membranes

In 2009, MTR began testing two types of polymeric membranes for pre-combustion applications: a CO_2-selective Polaris™ membrane and a hydrogen-selective Proteus™ membrane. Successful operation has led to scale-ups of both membrane types. In 2011, MTR scaled up the hydrogen membrane from a 1-lb/hr stamp cell to a 10-lb/hr module, and in 2013, incorporated a further scale up to 50 lb/hr. In 2012, MTR scaled up the 50-lb/hr CO_2 membrane module to an integrated system designed for 500 lb/hr syngas.

4.2.1 MTR 500-lb/hr CO_2 Membrane System

Based on successful 50 lb/hr module testing beginning in 2009, a membrane demonstration system for treating 500 lb/hr of syngas (equivalent to 0.15 MWe) was constructed and installed at NCCC in 2012. The integrated 500-lb/hr CO_2 membrane system consists of membrane, compressor, and refrigeration skids, which are shown in Figure 31 as installed at the SCU. This system was designed to test a membrane-assisted CO_2 liquefaction process.

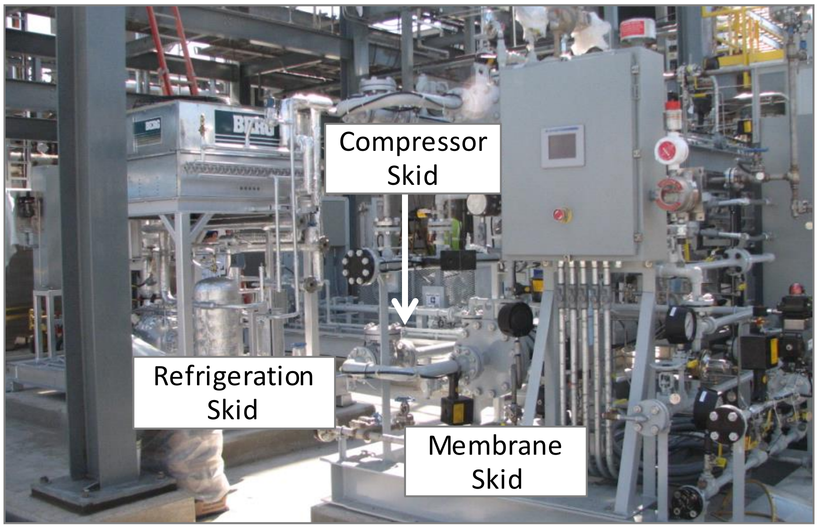


Figure 31. MTR 500 lb/hr Membrane System

The membrane skid includes two stages of membrane modules for CO_2 separation. The first membrane stage can accommodate one or two 8-inch diameter modules with a membrane area of up to 430 ft^2, and the second membrane stage holds one or two 4-inch diameter modules with a membrane area of up to 64 ft^2. The skid also houses a sulfur polishing reactor and two desiccant dryers for sulfur and moisture removal upstream of the compressor and refrigeration skids, heaters, and control panels. The first-stage permeate stream from the membrane skid is pressurized to about 420 psig in the compressor skid, and then the compressed gas stream is liquefied in the refrigeration skid which removes the CO_2. Uncondensed gas is fed to the second-stage membrane for further CO_2 separation. The second-stage membrane permeate stream is combined with the first-stage permeate stream, and the combined stream is treated in the sulfur polishing reactor. Reject streams from both first- and second-stage membrane modules, as well as the liquid CO_2 stream, are sent to the atmospheric syngas combustor. The overall system captures 70 percent of the CO_2 in the feed as high-pressure, high-density fluid ready for sequestration.

The system was commissioned and operated during R09 and subsequently operated during runs R10 and R11, with modifications made to the system after each run based on lessons learned. MTR achieved a total of 750 hours through these three runs, demonstrating improved reliability over time. During run R11, the first-stage membrane enriched CO_2 from 11.5 percent in the feed to 40 percent in the permeate stream, which was higher than the permeate CO_2 content in the R10 testing campaign (about 33 percent), due to the improved Polaris membrane modules. The membrane system continuously produced CO_2 at a purity of 95 percent or greater at -27^oF and 420 psig. The liquid CO_2 production rate also improved significantly in R11 to 35 to 40 lb/hr (from about 15 lb/hr during R09 testing), corresponding to a CO_2 capture rate of 60 to 70 percent. Figure 32 shows the CO_2 content in the liquid CO_2 stream and the feed gas as a function of time during R11.

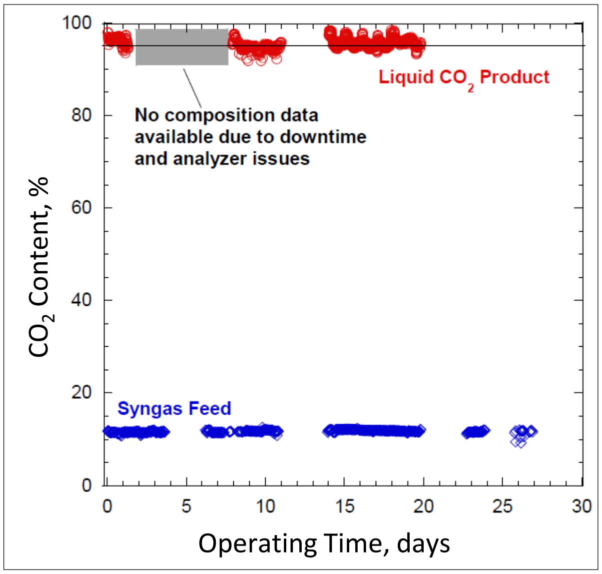


Figure 32. CO_2 Content of Inlet and Outlet Streams of the MTR 500-lb/hr Membrane System during R11

Table 8 records the results of three samples of measured liquid CO_2 stream compositions after the system was running at steady state for several hours, and compares these results with the predicted composition from a commercial CHEMCAD 6.3 process simulator. The liquid streams were at -22°F and 420 psig. In the simulation, the H_2S content in the feed gas entering the condenser was assumed to be 5 ppmv, and the Soave-Redlich-Kwong thermodynamic equation of state was used to describe the phase behavior of the gas mixture. As shown in the table, the measured and predicted values were fairly close.

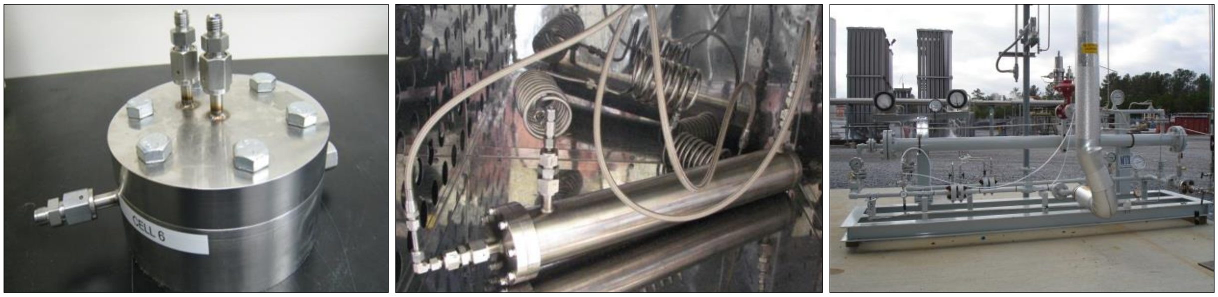
Table 8. Measured and Predicted Composition of Liquid CO_2 Stream of MTR 500 lb/hr Membrane System during R11

Component	*Measured Compositions of Liquid CO_2 Stream, mol%*			*Predicted Composition, mol%*
	Sample 1	*Sample 2*	*Sample 3*	
CO_2	94.36	97.43	99.00	98.52
N_2	3.67	1.34	0.32	1.26
CO	0.54	0.20	0.04	0.18
CH_4	0.09	0.06	0.01	0.03
H_2	0.56	0.19	0.01	0.01
H_2S	0.78	0.78	0.62	0.20

The operation of the 500 lb/hr syngas demonstration unit concluded in R11. It successfully demonstrated that an integrated Polaris CO_2 membrane-refrigeration system can reliably produce liquid CO_2 from coal-derived syngas. The successful operation of this system provides a baseline for future optimization and improvement.

4.2.2 MTR Bench-Scale CO_2 and Hydrogen Membranes

MTR's bench-scale systems are used as test vehicles to collect membrane performance data as development continues. Figure 33 shows the small-scale membrane test units.



1 lb/hr Stamp Cell
10 lb/hr Membrane Module
50 lb/hr Membrane Skid

Figure 33. MTR Small Scale CO_2 and Hydrogen Membrane Test Units

During R10, the Polaris CO_2 membrane was tested at 50 lb/hr for a total of 670 hours, and the Proteus hydrogen membranes were tested at 1 lb/hr for 582 hours. Testing of the small-scale CO_2 and hydrogen membranes was not performed during R11, as modifications to the CO_2 membrane test skid were underway to adapt it for hydrogen membrane testing.

During R10, a CO_2 membrane prepared as a semi-commercial module, which had been tested previously in R09, continued to operate stably and enriched CO_2 content fourfold, from about 10 percent in the feed to about 40 percent in the permeate stream. For the hydrogen-selective membranes, several membrane stamps were tested in R10, which enriched hydrogen content from about 10 to 80 percent. In addition, it was demonstrated that these Proteus membranes are resistant to sulfur components. One optimized Proteus membrane achieved H_2/H_2S selectivity of about 50, providing a reduction in the H_2S content of the H_2-enriched stream.

The first testing of MTR's hydrogen membrane at 50 lb/hr was conducted in R12. The membranes were tested as four-inch standard modules, shown in Figure 34, produced using a commercially representative manufacturing process. To test this scaled-up hydrogen membrane, MTR modified the existing 50 lb/hr CO_2 membrane skid at the NCCC for higher temperature operation. The modifications included the addition of a new syngas heater, heat tracing to keep the module and inlet, residual, and permeate streams at operating temperature, and new instrumentation. The hydrogen membrane operates at elevated temperatures, with both selectivity (H_2/CO_2, H_2/H_2S, etc.) and hydrogen permeance dependent on the system temperature. Membrane performance improves substantially above 212°F, while the best performance takes place between 257°F and 302°F.

Figure 34. MTR's Hydrogen Membrane Modules Tested in R12

During the R12 run, the two hydrogen membrane modules operated for a combined 417 hours without leaks, verifying MTR's manufacturing scale-up protocols. However, skid temperature control issues during testing resulted in lower than expected module performance in hydrogen permeance and selectivity. Changes to the heat tracing will be made prior to additional testing planned for 2014.

4.3 Media & Process Technology Membrane

Media & Process Technology, a technology innovator specializing in the development of high-performance, low-cost ceramic membranes, first tested its hydrogen-selective Carbon Molecular Sieve (CMS) membrane at the site in 2008. MPT began evaluation of the CMS technology with single tubes, progressing to a pilot bundle containing 14 tubes before developing a full-scale 86-tube bundle with a total surface area of 8.2 ft^2 processing up to 50 lb/hr of syngas. The bundle consists of 86 alumina tubes contained within a 5-inch diameter pressure vessel and is designed for operating temperatures as high as 570˚F and transmembrane pressure drops of over 300 psi. Since successfully demonstrating the full-scale CMS in 2012, MPT has incorporated the WGS functionality into the CMS bundle to produce a catalytic membrane reactor (CMR). This concept allows the separation of hydrogen simultaneously with its formation.

For R10, MPT tested the catalytic membrane reactor concept by installing WGS catalyst inside the CMS vessel surrounding the membrane bundle. The WGS catalyst had been crushed and sieved to 1,000 to 450 microns and placed into the CMS vessel, completely filling the internal space. Initial testing with the tightly packed catalyst next to the membrane bundles resulted in tube failure. Further testing with the vessel only partially filled with the catalyst, leaving two to three inches of space at the top, was conducted without tube failures.

A total of 380 testing hours was completed during R10. Raw syngas from PRB coal with around 8 vol% moisture was fed at 50 lb/hr with the reactor conditions held at 200 psia and 500°F. No additional steam or hydrogen was added to the syngas. At the conditions tested, approximately 25 percent of the CO was shifted to hydrogen, and the membrane flux remained stable. The CO conversion rate was lower than expected, possibly due to the low H_2O-to-CO ratio. Following the run, a steam line was added to increase this ratio.

MPT further evaluated the CMR in run R11, completing 350 hours of operation without any membrane tube failure. On average, CO conversion was 50 percent with the moisture inherent in the syngas, and there was no reduction in membrane permeance. The higher CO conversion was attributed to the higher inherent moisture content in syngas from the lignite coal used in R11 compared to that from the PRB coal used for R10. Though a new steam line was added before

R11, it was not put in service due to condensation issues in the line. Continued testing of the CMR, originally planned for the R12 run but delayed due to a valve failure, will be conducted in run R13.

4.4 TDA Research Sorbent

Technology developer TDA Research is advancing a new pre-combustion CO_2 capture technology that uses a proprietary carbon-based sorbent modified with surface functional groups to physically adsorb CO_2 from shifted syngas. TDA Research tested the sorbent during R07 in November 2011, utilizing about 5 lb/hr sweet, shifted syngas. The group modified the process to combine the WGS reaction and sorbent CO_2 capture in the same reactor for testing in run R10. The integrated operation of the WGS catalyst and CO_2 removal processes in a single step drives the equilibrium-limited WGS reaction towards hydrogen without the need to add large amounts of steam to the syngas, greatly reducing the cost of carbon capture.

To accommodate the testing, the NCCC installed a new syngas line to deliver untreated syngas (sour and un-shifted) to the TDA skid, which is shown in Figure 35. In addition, NCCC provided deionized water for TDA to use in its steam generator for the WGS reaction. TDA used its own WGS reactor and the combined WGS catalyst and CO_2 sorbent to study the interaction between the WGS reaction and CO_2 adsorption.

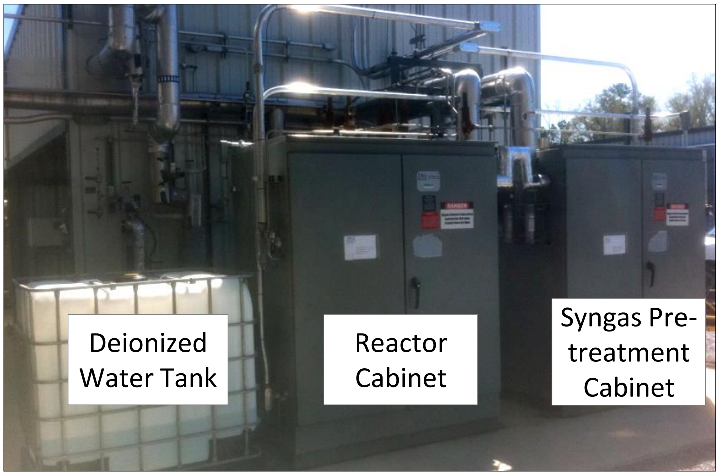


Figure 35. TDA Research Sorbent System

During the run, TDA completed 384 hours of testing using 3.5 lb/hr of untreated syngas, demonstrating high CO conversions (greater than 96 percent) at steam-to-CO ratios of less than 1.2. As charted in Figure 36, the CO conversion at a steam-to-CO ratio of 1.1 was over 5 percent more than that predicted at a temperature of 230°C (446^{o}F). This shift in equilibrium was likely due to the closely coupled removal of the CO_2 product gas, which enabled the WGS reaction to further approach completion. The lower than equilibrium CO conversion at a steam-to-CO ratio of 1.0 was possibly due to the adsorption of CO on the sorbent. Since 20 percent of the bed at the syngas inlet was pure sorbent, a portion of CO was picked up in this section before reaching the catalyst.

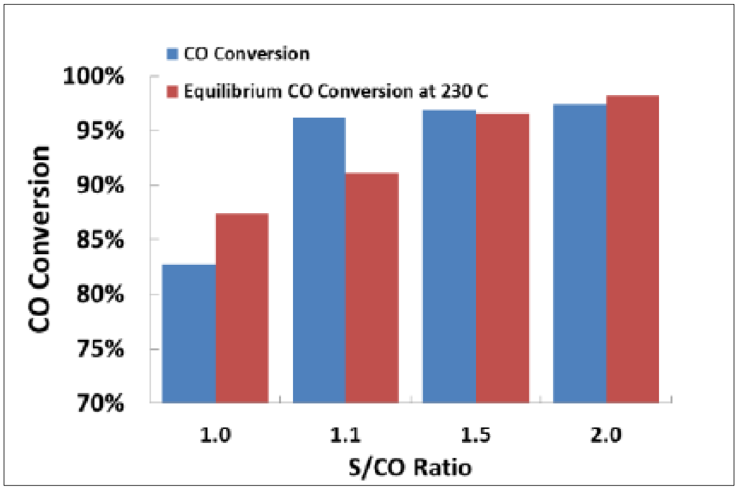


Figure 36. Conversion of CO with TDA Research Sorbent and Equilibrium CO Conversion at Various S/CO Ratios

The testing also showed that combining the WGS catalyst with the CO_2 sorbent did not adversely affect the sorbent CO_2 capacity. At low steam-to-CO ratios, the capacity improved due to the lower partial pressure of H_2O. The CO_2 capture rate was maintained at greater than 96 percent.

TDA plans to redesign its WGS/CO_2 sorbent reactor for improved thermal management and return for testing in 2014.

4.5 University of Alabama Solvent

The Bara Research group of the University of Alabama (UA) has been researching the use of alkylimidazoles, a group of low volatility and low viscosity liquids, as physical solvents for economical CO_2 separation from processes like IGCC. The NCCC conducted a series of tests on two solvents, 1-methylimidazole (MEI) and 1,2-dimethylimadizole (DMI), provided by UA to measure CO_2 and H_2S absorption in the SCU batch reactor. These tests included bottled gas mixtures of nitrogen and CO_2 and syngas generated during runs R09 and R10.

The absorption of CO_2 from syngas as a function of time at 150 psig is shown in Figure 37. The CO_2 in the syngas was supplemented with bottled CO_2 to achieve a partial pressure of about 50 psi. CO_2 was rapidly absorbed, and complete saturation with CO_2 was observed after 10 to 20 minutes. Three curves are shown in Figure 37 that represent used MEI, used MEI plus 20 percent DMI, and fresh MEI plus 20 percent DMI. Fresh solvent did appear to have slightly higher CO_2 capacity than used solvent, but this difference disappeared after a single test.

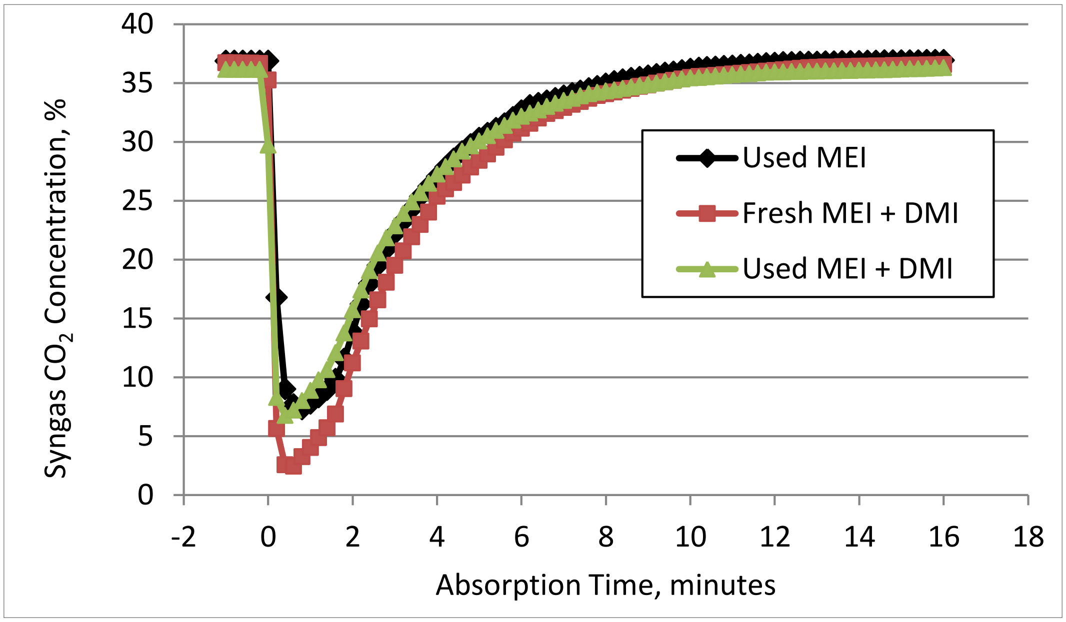


Figure 37. CO_2 Absorption versus Time for UA Solvents

The total CO_2 capacity of the MEI solvent is plotted as a function of CO_2 partial pressure in Figure 38. These measurements were made with bottled gas so that higher partial pressures could be reached. Also shown are the results for the other physical solvents that have been tested at NCCC, including dimethyl ether of polyethylene glycol (DEPG), glycerol triacetate (GTA), and polydimethyl siloxane (PDMS). The MEI fell in the range of the other solvents.

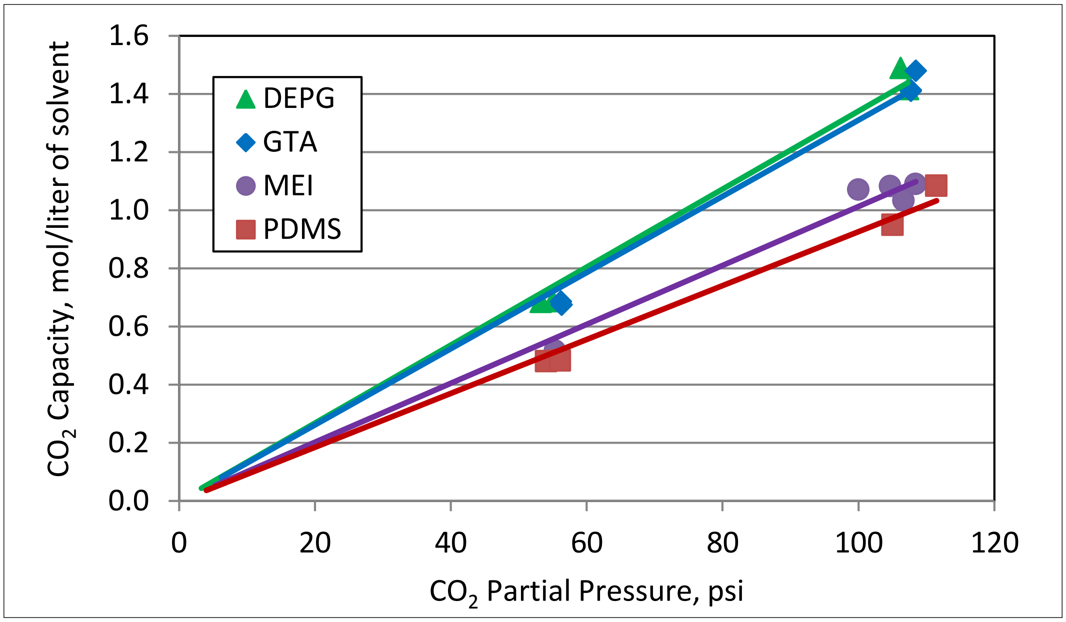


Figure 38. CO_2 Capacity of UA Solvent and Other Physical Solvents

Figure 39 compares the CO_2 capacity measured with syngas to the bottled gas data from the previous figure. Data are shown for 100 percent MEI, for MEI with 10 percent water addition, and with a mixture of 20 percent DMI in MEI. All of the syngas data appeared to be slightly better than the bottled gas curve, but the difference was not significant. For the case with water addition to the MEI, only the quantity of the MEI was used for calculating the amount of solvent. For the mixture of the two solvents, the total amount of both was used. The water diluted the MEI, but did not interfere with CO_2 absorption by the remaining MEI, as some solvent water mixtures have. Addition of 20 percent DMI did not change the CO_2 capacity of the mixture.

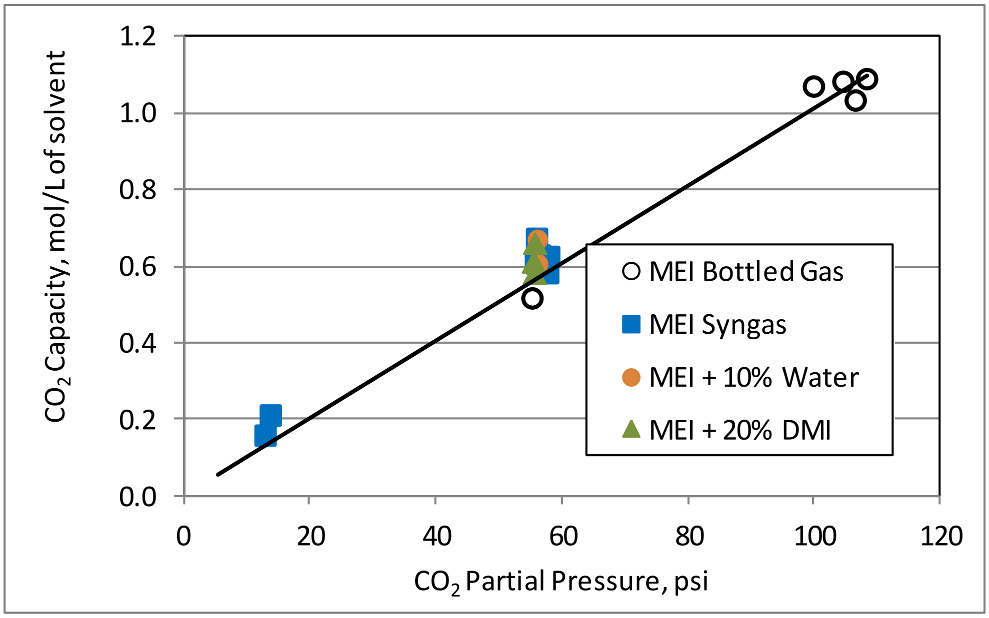


Figure 39. Comparison of Syngas and Bottled Gas Data for UA Solvent

When operating with syngas, the UA solvent also removed H_2S. The fresh undiluted solvent was saturated with CO_2 after about 20 minutes but this did not affect H_2S absorption until after 70 minutes when it too approached saturation. Flash regeneration released all the CO_2 from the sample but was not very effective at removing H_2S. This was indicated by the reduced H_2S absorption achieved in the second run, which reached saturation after 15 minutes. These results suggest that the H_2S reacts chemically and irreversibly with the solvent. The solvent is 99 percent pure, and the reaction may involve the contaminants present.

Variations of the flash technique were tried to improve the H_2S release. For the standard flash regeneration (see Figure 40) the saturated solution was slowly depressurized while being stirred and maintained at absorption temperature. One variant was to release the pressure more rapidly and another was to bubble nitrogen through the depressurized solvent. The only improvement noted was when a regenerated solution was used following a month of storage, but the improvement was not marked.

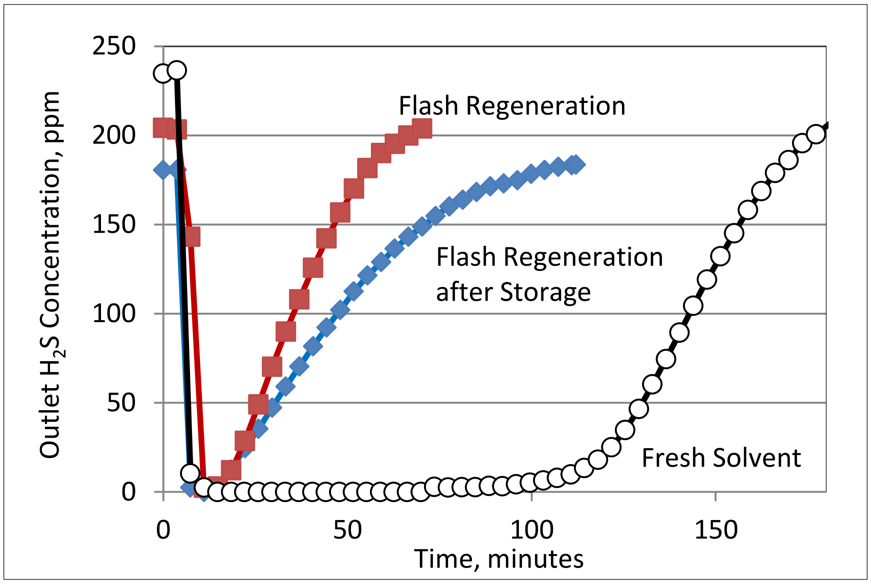


Figure 40. H_2S Concentration of UA Solvents during Regeneration

4.6 NETL Solvent

Testing of the hybrid siloxane (HSX) physical solvent supplied by NETL was conducted using bottled gases and then with syngas during run R12. The capacity of the solvent was determined at 70°F with 35 percent CO_2 in nitrogen and 165 and 315 psia (CO_2 partial pressure of 50 and 100 psi). The data are plotted in Figure 41 along with data at 70^{o}F for DEPG and PDMS collected in previous test runs. For HSX, the two high points at about 100 psi were measured after the regenerated solvent sat overnight, while the lower one was run immediately after regeneration. This may indicate a slow release of CO_2 similar to that of the UA solvent.

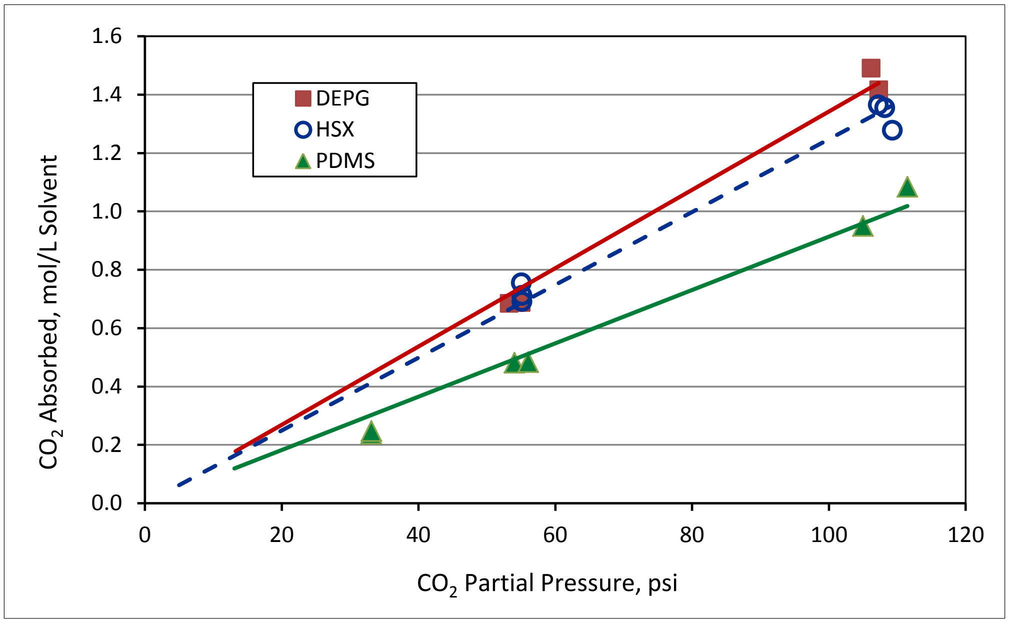


Figure 41. Absorption of CO_2 for Hybrid Siloxane, DEPG, and PDMS Solvents

Figure 42 includes absorption data from syngas operation. The HSX exhibited a similar CO_2 loading capacity to DEPG.

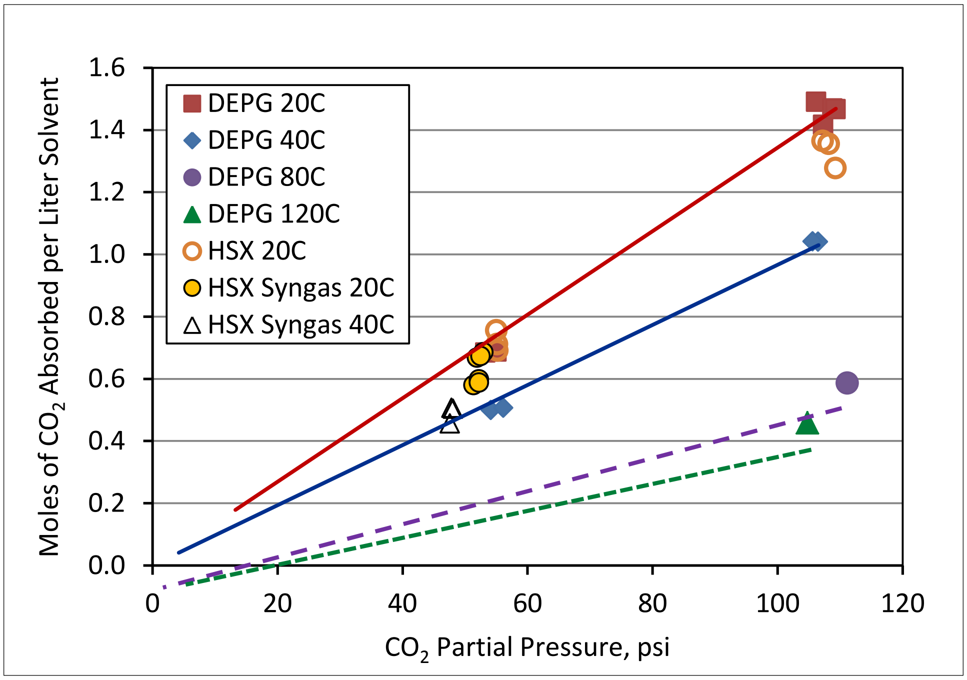


Figure 42. Absorption of CO_2 for Hybrid Siloxane and DEPG Solvents at Varying Temperatures

Operation with the solvent resulted in the formation of a very fine aerosol during absorption, which has not been the case for other solvents tested. Liquid collected in the exit piping indicated that measurable amounts of solvent were carried over during absorption. To desorb the solvent, the pressure was reduced with the stirrer operating. The solvent was then poured into a container to determine solvent losses during the absorption/regeneration process. From the pouring, about one inch of foam was generated on the surface of the solvent, indicating that additional CO_2 was being released.

4.7 Syngas Conditioning Unit Modifications

In 2012, the SCU was expanded to include a new syngas cleaning system with a capacity of 1,000 lb/hr to support larger scale technology testing, providing sulfur and hydrocarbon removal. During 2013, reactor vessels were installed for WGS and COS hydrolysis, and piping and detail design for these additions are to be completed in 2014. Various minor modifications to the cleaning system were also incorporated in 2013, such as increasing the scrubber vessel capacity, based on initial operating experience. Figure 43 provides a view of the syngas cleaning system with the new reactor vessels.

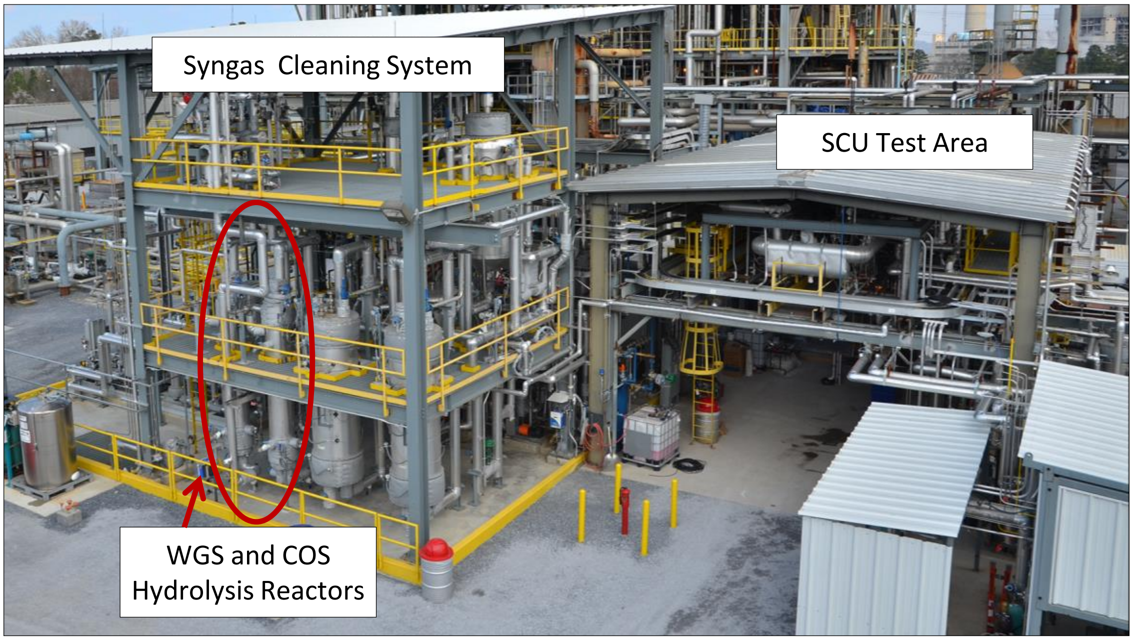


Figure 43. SCU with Syngas Cleaning System

5.0 CONCLUSIONS AND LESSONS LEARNED

5.1 Post-Combustion

Akermin Enzymes

Akermin completed a successful test campaign at PC4 with more than 3,500 hours testing the immobilized carbonic anhydrase enzyme-based system. Testing demonstrated:

- More than 2,800 hours on coal flue gas with steady performance of about 80 percent CO_2 capture using potassium carbonate solvent
- 700 hours of operation with the AKM-24 solvent, with 90 percent capture at design conditions
- Low solvent loss due to heat stable salt build up (less than 1.6 percent per year)
- Aerosol emissions lower than detection limit of 0.8 ppm
- High purity (greater than 99 percent) CO_2 production
- Negligible detectible corrosion rates using 304-stainless steel
- Energy consumption of about 3.5 GJ/ton CO_2 with the Akermin process using K_2CO_3 as absorption solvent

Chiyoda Solvent

Chiyoda began testing its T-3 solvent in the PSTU in December 2012 and completed testing in June 2013, for about 1,500 hours of operation. Operation with the Chiyoda solvent included 24 test conditions, and mass balances were completed for each condition with 97 percent or higher closures. Chiyoda is completing data analysis and will report the results once finalized.

Cansolv Technologies Solvent

Testing of the Cansolv DC-201 solvent under natural gas flue gas simulated conditions was completed after 1,715 hours of operation in the PSTU. Initial tests varied the liquid-to-gas ratio in the absorber and steam flow rates to the regenerator to identify the operating conditions for the long-term solvent degradation test. Long-term testing was focused on solvent performance, degradation, and emissions. Results of corrosion studies will be reported once finalized. Accomplishments of the Cansolv testing include:

- Maintained process performance near 90 percent CO_2 removal for the duration of the testing
- Demonstrated a limited influence of transformation product concentration on CO_2 removal
- Demonstrated a maximum increase in overall energy consumption (stripping factor) of about 10 percent without intercooling or energy integration

- Completed solvent emissions testing showing 33 times greater emissions with natural gas simulated flue gas and 77 times greater emissions with typical coal flue gas over emissions with ambient air

MTR 1-ton/day Flue Gas Membrane

MTR continued operation of the 1-TPD unit, accumulating a total of 3,522 hours of operation in 2013. Of this, about 1,800 hours of operation were conducted with typical flue gas conditions while 1,300 hours were with diluted flue gas. The balance of operating hours were conducted using air when flue gas was not available and when purging was required. MTR operated with a newly installed compressor and with several new cross-flow and sweep air modules.

The modules tested during the year demonstrated stable performance at expected levels of separation, even after periods when the system was idle for repair/maintenance and PC4 outages. The system consistently demonstrated 90 percent CO_2 capture with typical flue gas. While operating with diluted flue gas, the system still performed well, with more than 80 percent CO_2 capture and an almost 8-fold CO_2 enrichment in the permeate stream.

Analysis of cross-flow modules tested from December 2011 through July 2013 showed that both CO_2 permeance and CO_2/nitrogen selectivity remained almost unchanged (within the error range of the pure-gas module testing system), even after repeated system start-ups, shutdowns, and idle periods. MTR found that fouling of membrane from condensation of water containing ammonium bisulfate can be avoided by purging the system with fresh air before shutting down the system. This finding specifically gained from this field testing is significant for extending the lifetime of the membrane in a commercial setting.

SRI International Sorbent

SRII completed design and fabrication of the sorbent test unit, which was installed at the PC4 in October. With commissioning and initial operation of the unit with flue gas, SRII personnel identified and incorporated minor design changes to improve operation. Testing of the sorbent unit will resume in the first quarter of 2014 for a planned duration of 1,000 hours.

MTR 20-ton/day Membrane System

MTR will test a 1-MWe-scale, 20-TPD CO_2 membrane test skid based on the 1-TPD CO_2 system test results. During 2013, MTR completed the detailed design and initiated fabrication of the scaled-up system, and the NCCC installed the needed foundation at the PC4. Delivery and commissioning is expected in the second quarter of 2014, with testing to begin soon thereafter.

Linde-BASF Solvent and Process

Linde and BASF will operate 1-MWe CO_2 capture pilot plant processing up to 30 tons CO_2 /day at the PC4 beginning in 2014. Linde-BASF completed detailed design, and fabrication of the process modules was completed by the end of the year. The NCCC finalized site preparations, including a foundation and sump system, and installed utility tie-ins and solvent handling and storage systems.

PC4 Upgrades

To meet the requirements of future testing at the PC4, work was in progress to increase the overall capacity. The NCCC installed a new blower, structured packing in the pre-scrubber, electrical infrastructure, and a new cooling tower cell, and will complete the project in 2014 with installation of a new pre-scrubber for the bench-scale area. NCCC also continued work on the SSTU, finalizing the design of needed modifications and installing the module and major components.

Engineering Studies

The NCCC's Engineering and Economic Evaluations group completed a PCC baseline study and sent a draft report to NETL. The study included three cases: a PC plant without CO_2 capture; a PC plant with 90 percent capture using MEA; and a PC plant with 50 percent capture using MEA. The group also worked with ChemStations and DOE to have a unit operations block for membranes developed for CHEMCAD process simulation software, and the unit block will be included in ChemStations next release of CHEMCAD.

5.2 Gasification

Gasification Operation

The gasification process operated over three test runs, R10, R11, and R12, for a total of more than 2,000 hours. The feedstock for runs R10 and R12 was Powder River Basin (PRB) coal, and for R11, Mississippi lignite from the Liberty Fuels mine in Kemper County was used. At the conclusion of R12, the gasification process had operated for over 20,000 hours. Operation was stable, with high carbon conversions and consistent quality syngas for use in gasification and pre-combustion tests.

Sensor Development

Modifications to the Emerson sapphire thermowell previously tested in the gasifier were successful in preventing measurement drift. Collaboration is ongoing with SWR Engineering to improve the Densflow coal flow meter. The Dynatrol vibration level probes and a point sensitive level probe from Drexelbrook used in controlling the developmental feeder continued to provide reliable measurements.

Hot Gas Filter Operation

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

WGS and COS Hydrolysis Catalysts

Through the end of 2013, testing of a developmental WGS catalyst had encompassed more than 3,500 hours of syngas operation, with no significant degradation of the catalyst. Operation was typically conducted at a syngas flow rate of 50 lb/hr, a temperature of 480^oF, a pressure of 180 psig, and a steam-to-CO ratio of 1.0 (using only the steam inherent in the syngas). Parametric testing of the WGS catalyst with syngas produced from PRB coal and lignite showed that, in the range tested, the temperature did not significantly affect CO conversion. Lower space velocity achieved by reducing the syngas flow rate to 25 lb/hr increased the conversion to slightly above estimated equilibrium values. The higher moisture content of the lignite coal compared to PRB coal resulted in higher CO conversion.

The same catalyst developer also provided a COS hydrolysis catalyst made with a honeycomb configuration, which was tested in R12 for about 400 hours. Further testing is planned for 2014 of both the WGS and COS hydrolysis catalysts.

Johnson Matthey Mercury Sorbent

For the R10 run, the NCCC installed a new reactor for continuous sorbent evaluation at a syngas flow rate of 50 lb/hr, and the mercury sorbent with 2 wt% palladium was tested for 490 hours at 400°F. Operation continued to show excellent capture of mercury and other metals. A study conducted during the run indicated that the catalyst did not promote WGS reaction.

OSU's Syngas Chemical Looping

The OSU process was installed, and commission began. The process will operate with syngas in 2014.

5.3 Pre-Combustion

WPI Hydrogen Membranes

WPI tested five membranes with various palladium and palladium/alloy compositions in 2013 for a total of 1,331 hours. The hydrogen produced during testing was typically above 99.5 percent in purity, except for two periods of testing when leaks occurred. WPI is continuing work on scaling up its membrane process.

To verify its laboratory results showing higher resistance to sulfur poisoning with the palladium/gold alloy, WPI conducted testing during the R10 run with this alloy adding controlled amounts of hydrogen sulfide (H_2S). The bottled H_2S was added to syngas at increments of 0.2, 0.3, and 0.5 slpm, corresponding to 3.7, 5.0 and 9.4 ppmv H_2S concentration in the membrane feed gas. Data showed that hydrogen permeance was reduced by 40, 48, and 60 percent at these respective H_2S concentrations. However, after the H_2S addition was stopped, the membrane permeance was fully recovered within 30 minutes. A repeated test confirmed the initial results. The remarkably quick recovery of hydrogen permeance following H_2S exposure and poisoning had not been reported before.

WPI Hydrogen Membranes

WPI continued to optimize the composition of its palladium-based membranes and demonstrated production of 99.9 percent pure hydrogen. WPI continues to investigate the cause of hydrogen flux decrease seen from test results, which appears to be related to carbon deposition on the membrane surface.

MTR 500-lb/hr CO_2 Membrane System

During run R11, the first-stage membrane enriched CO_2 from 11.5 percent in the feed to 40 percent in the permeate stream, which was higher than the permeate CO_2 content in the R10 testing campaign (about 33 percent), due to the improved Polaris membrane modules. The membrane system continuously produced CO_2 at a purity of 95 percent or greater at -27^{o}F and 420 psig. The liquid CO_2 production rate also improved significantly in R11 to 35 to 40 lb/hr (from about 15 lb/hr during R09 testing), corresponding to a CO_2 capture rate of 60 to 70 percent. MPT Hydrogen Membrane

MTR Bench-Scale CO_2 and Hydrogen Membranes

During R10, the Polaris CO_2 membrane was tested at 50 lb/hr for a total of 670 hours, and the Proteus hydrogen membranes were tested at 1 lb/hr for 582 hours. The CO_2 membrane continued to operate stably and enriched CO_2 content fourfold, from about 10 percent in the feed to about 40 percent in the permeate stream. The hydrogen-selective membranes enriched hydrogen content from about 10 to 80 percent. In addition, it was demonstrated that these Proteus membranes are resistant to sulfur components. One optimized Proteus membrane achieved H_2/H_2S selectivity of about 50, providing a reduction in the H_2S content of the H_2-enriched stream.

The first testing of MTR’s hydrogen membrane at 50 lb/hr was conducted in R12. The two membranes were tested as four-inch standard modules, produced using a commercially representative manufacturing process. The two hydrogen membrane modules operated for a combined 417 hours without leaks, verifying MTR’s manufacturing scale-up protocols. However, skid temperature control issues during testing resulted in lower than expected module performance in hydrogen permeance and selectivity. Changes to the heat tracing will be made prior to additional testing planned for 2014.

MPT Hydrogen Membrane

For R10, MPT tested the catalytic membrane reactor concept by installing WGS catalyst inside the CMS vessel surrounding the membrane bundle. Initial testing with tightly-packed catalyst next to the membrane bundles resulted in tube failure. Further testing with the vessel only partially filled with the catalyst, leaving two to three inches of space at the top, was conducted without tube failures. MPT completed 380 hours of testing, with about 25 percent CO conversion.

MPT further evaluated the CMR in run R11, completing 350 hours of operation. On average, CO conversion was 50 percent with the moisture inherent in the syngas, and there was no reduction in membrane permeance. The higher CO conversion was attributed to the higher inherent moisture content in syngas from the lignite coal used in R11 compared to that from the PRB coal used for R10.

University of Alabama CO_2 Solvents

The NCCC conducted a series of tests on two solvents, 1-methylimidazole (MEI) and 1,2-dimethylimadizole (DMI), provided by UA to measure CO_2 and H_2S absorption in the SCU batch reactor. Syngas data was collected for MEI and for MEI with added DMI. The CO_2 capacity was in the range of other physical solvents tested previously. Absorption and regeneration tests of the MEI showed that fresh solvent removed much more H_2S than did used solvent. Thermal regeneration at temperatures up to 212°F did not remove H_2S, although various methods of flash regeneration were successful at removing some H_2S. The H_2S absorption appeared to be an irreversible reaction with some component of the solvent.

NETL CO_2 Solvent

Testing of the hybrid siloxane (HSX) physical solvent supplied by NETL was conducted in the SCU batch reactor using bottled gases and then with syngas during run R11. The HSX exhibited a similar CO_2 loading capacity to DEPG. Operation with the solvent resulted in the formation of a very fine aerosol during absorption, which has not been the case for other solvents tested.

SCU Modifications

During 2013, modifications to the new 1,000 lb/hr syngas cleaning system were incorporated, including installation of WGS and COS hydrolysis reactor vessels and minor changes made to improve operation.