The National Carbon Capture Center at the Power Systems Development Facility Test Run Summary Report

Test Run R10
March 20, 2013 – April 23, 2013

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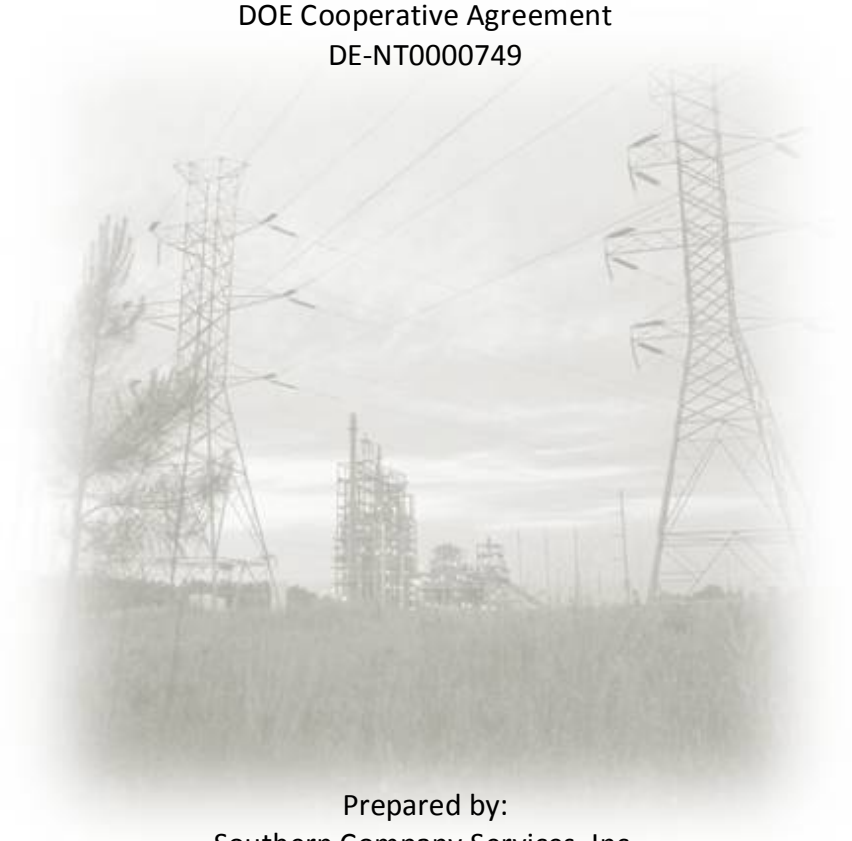

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List of Abbreviations

CCAD	Continuous Coarse Ash Depressurization
CFAD	Continuous Fine Ash Depressurization
CMR	Catalytic Membrane Reactor
CMS	Carbon Molecular Sieve
DOE	Department of Energy
EPRI	Electric Power Research Institute
MPT	Media & Process Technology
MTR	Membrane Technology & Research
NCCC	National Carbon Capture Center
PCD	Particulate Control Device
PDAC	Pressure Decoupled Advanced Coal
PRB	Powder River Basin
PSDF	Power Systems Development Facility
SCS	Southern Company Services
SCU	Syngas Conditioning Unit
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 (DOE), the PSDF is an engineering scale test center located in Wilsonville, Alabama. Since operation began in 1996, the PSDF staff has effectively developed advanced power systems, moving innovative technologies into the marketplace. Building on its previous success, PSDF now hosts the National Carbon Capture Center (NCCC) to address the nation's need for commercially viable CO_2 capture options for flue gas from pulverized coal power plants and syngas from coal gasification power plants.

Gasification test run R10 took place from March 20 through April 23, 2013, for a total run duration of 825 hours. Progress continued on the development of the pressure decoupled advanced coal (PDAC) feeder, gasifier control automation, instrumentation, and hot gas filtration. Operation of the gasification process also supported testing of syngas conditioning and pre-combustion technologies, including a mercury sorbent, a water-gas shift (WGS) catalyst, gas separation membranes, a CO_2 sorbent, and CO_2 solvents. At the conclusion of R10, the gasification process had operated for a total of almost 19,000 hours.

2.0 COAL PREPARATION AND FEEDING

The coal used for R10 was Powder River Basin (PRB) sub-bituminous coal, which was processed in the mill system to achieve the desired moisture concentration and particle size distribution. A total of 1,635 tons of PRB coal were processed. Table 1 lists the average coal properties as-received and as-fed (after processing in the coal mill).

Table 1. PRB Coal Properties.

Coal Property	Value
As-Received Carbon, wt %	49.4
As-Received Hydrogen, wt %	3.2
As-Received Nitrogen, wt %	0.7
As-Received Sulfur, wt %	0.2
As-Received Ash, wt %	5.3
As-Received Oxygen, wt % (by difference)	11.1
As-Received Volatiles, wt %	29.2
As-Received Fixed Carbon, wt %	35.3
As-Received Heating Value, Btu/lb	8,290
As-Received Moisture Concentration, wt%	30
As-Fed Moisture Concentration, wt%	22
Moisture Content Reduction, %	27
As-Fed Mass Median Diameter, micron	384
As-Fed Oversize (>1,180 micron) Content, wt%	9.6
As-Fed Fine (< 45 micron) Content, wt%	9.7

Both the developmental PDAC feeder and the original rotary coal feeder operated during R10 without any major coal stoppages. The PDAC feeder operated for 737 hours during the run at coal feed rates ranging from 930 to 3,880 lb/hr, and the original feeder operated for 747 hours at feed rates varying from 872 to 2,117 lb/hr. Overall, feeder performance during the run was stable over the range of coal feed rates tested.

PDAC Control Logic and Instrumentation

Testing of previous control logic improvements continued during the run. The coal feed rate trim controller successfully maintained a consistent coal feed rate to the gasifier by changing the nitrogen feed rate to the feeder as necessary.

The solids level probes in the PDAC feeder continued to perform reliably. The Dynatrol vibration level probes installed in the PDAC feeder dispense vessel and lock vessel have operated for more than 6,785 hours. The Drexelbrook point sensitive level probe, which is vertically installed in the top of the PDAC feeder dispense vessel, has been in operation for more than 5,585 hours.

Operation with the DensFlow coal flow meter continued to show discrepancy in coal feed rates from the weigh cell calculation and the flow meter. Figure 1 plots the PDAC feed rate indicated by both methods. Further collaboration with SWR Engineering personnel is needed to improve the flow meter performance.

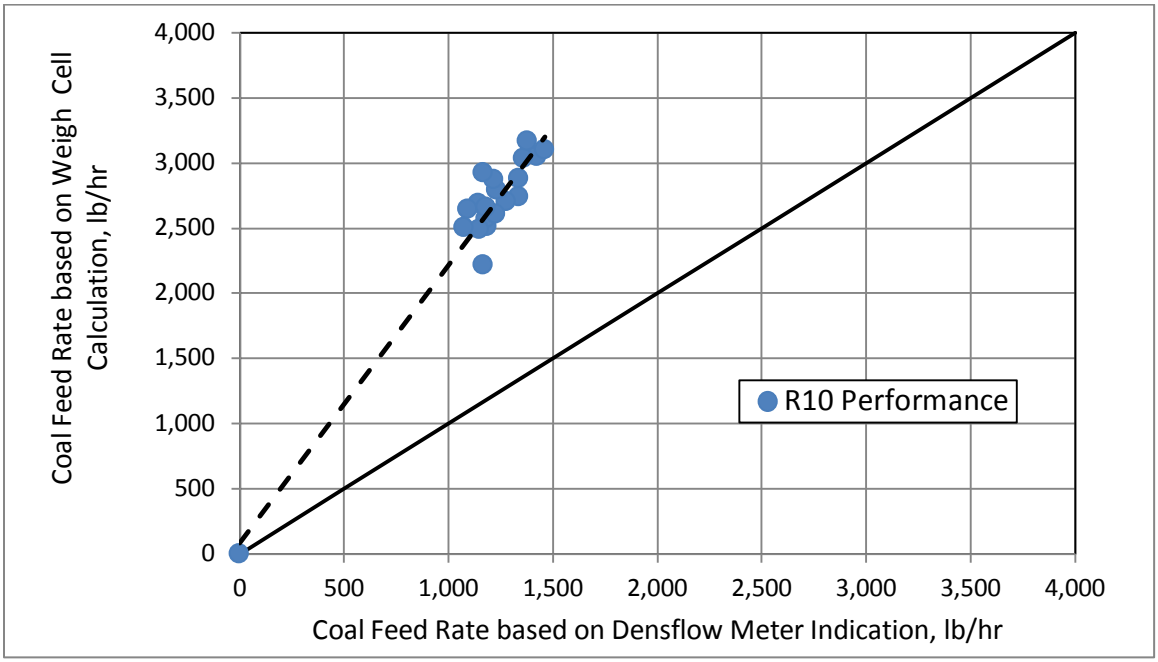

Figure 1. Comparison of Weigh Cell Calculated Feed Rate and Densflow Meter Indication.

3.0 TRANSPORT GASIFIER

R10 operation consisted of 78 steady state operating periods, with recycled syngas utilized for gasifier fluidization during all periods. Gasifier operation during the run yielded high carbon conversions, as shown in Table 2. The historical figures for carbon conversion represent data collected since completion of the 2006 gasifier modifications. Gasifier temperature control enhancements utilizing air flow adjustments from the gasifier upper and lower mixing zone continued through incremental tuning improvements.

Table 2. Steady-State Carbon Conversion for R10 and Previous PRB Test Runs.

	Maximum	Minimum	Average
R10 Carbon Conversion	99.9	98.6	98.9
Historical PRB Carbon Conversion	99.6	95.3	98.4

Figure 2 plots the maximum gasifier temperature (the mixing zone temperature), the outlet gasifier temperature and pressure, and the primary gas cooler outlet temperature during the steady state periods. The primary gas cooler operated as designed, with an outlet temperature of about 800°F during the run.

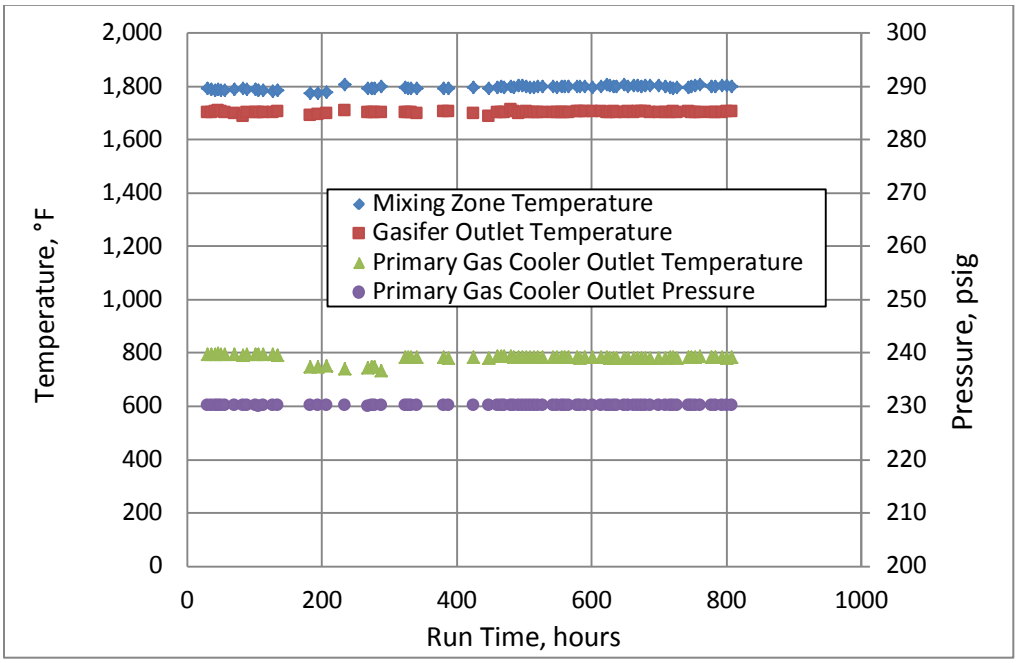

Figure 2. Gasifier Operating Conditions.

Gasifier Refractory Inspections

Gasifier system inspections did not reveal any significant refractory degradation. The gasifier standpipe installed in 2012 continued to demonstrate excellent refractory performance. Refractory in the mixing zone and J-leg intersection continued to show minimal additional wear with an acceptable thickness of hard-face refractory remaining.

4.0 PARTICULATE CONTROL DEVICE

The Particulate Control Device (PCD) operated with a high collection efficiency and stable pressure drop with particulate outlet loading typically less than 0.1 ppmw. Long-term material evaluation of the filter elements continued. The elements with the longest exposure time are Iron Aluminide, which after 17,000 hours of operation following R10, continued to demonstrate minimal pressure drop across the filter media.

5.0 SYNGAS CONDITIONING AND PRE-COMBUSTION CO_2 CAPTURE TECHNOLOGIES

5.1 Johnson Matthey High Temperature Mercury Sorbent

During R10, the Johnson Matthey palladium-based mercury sorbent with 2 wt% palladium was tested for 490 hours at 400°F with 50 lb/hr of sour syngas. 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 whether there was 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 3. No breakthrough was detected, so only the inlet concentrations are given.

Table 3. Metals Concentrations during Mercury Sorbent Test.

Date	Mercury		Arsenic		Selenium	
	μg	μg/Nm^3	μg	μg/Nm^3	μg	μg/Nm^3
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 staff used gas chromatography analysis on the outlet 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 to analyze the mercury, selenium, and arsenic.

5.2 Water-Gas Shift Catalyst

Data collected with the WGS catalyst tested in R10 are presented in Figure 3 along with data collected in previous runs. While this catalyst type has been tested in runs R07 through R10, this particular batch of catalyst was first installed in R08, and it has accumulated close to 1,800 hours of syngas exposure. Testing will be completed in R11 with the same batch for an expected total of around 2,500 hours of exposure. The catalyst vendor wishes to test a COS hydrolysis catalyst starting in R11 for a comparable number of hours.

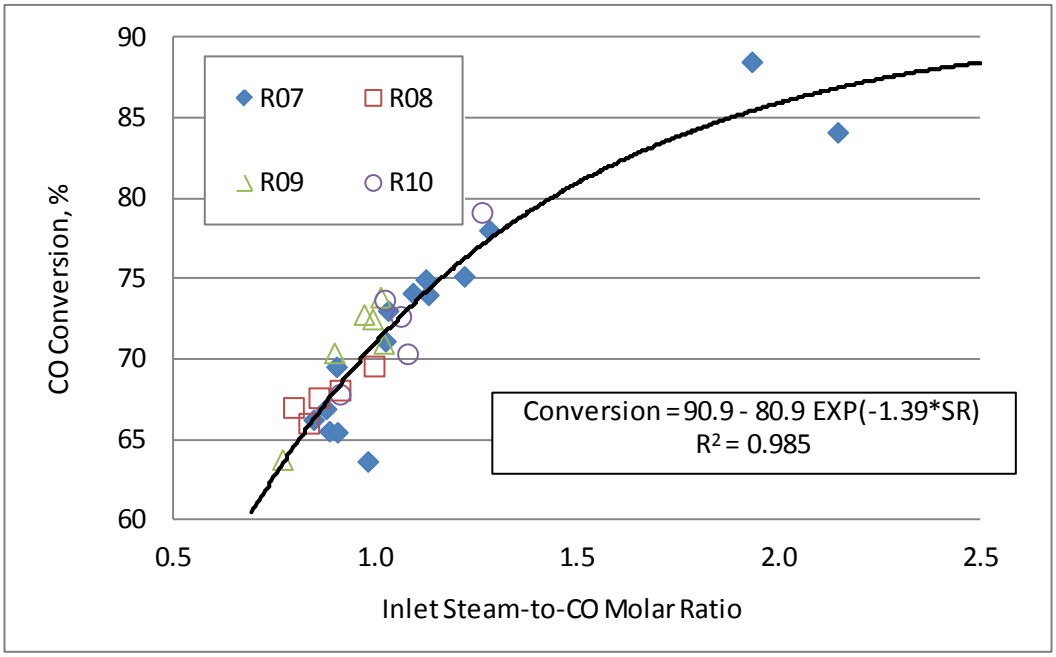

Figure 3. CO Conversion for WGS Catalyst Testing in Runs R07 through R10.

5.3 Worcester Polytechnic Institute Membranes

Two of Worcester Polytechnic Institute's (WPI's) palladium-based hydrogen membranes were tested in R10 for a combined 486 hours. The first membrane, palladium-only, was tested for a total of 233 hours (179 hours on syngas) before a leak developed and the test stopped. The second membrane used a palladium-gold alloy that was shown in laboratory testing to have better resistance to sulfur poisoning. To test the effect of sulfur on performance, the NCCC spiked the syngas with hydrogen sulfide (H_2S) during the 253 hours test run (230 hours on syngas). No leaks developed, and hydrogen purity in the permeate stream was near 100 percent for the entire period.

During start-up, the membrane assembly was heated in the oven with 10 lb/hr of nitrogen flowing through the membrane. Once the operating temperature of 840°F was reached, 0.22 lb/hr of hydrogen was introduced into the inlet nitrogen. Once stable operation was achieved, the nitrogen was switched to 10 lb/hr of shifted, desulfurized syngas while maintaining the same hydrogen flow to establish baseline performance before H_2S addition.

H_2S from gas cylinders (1,600 ppmv H_2S in nitrogen) was introduced into the syngas downstream of WPI's sulfur polishing bed using a newly installed gas supply line. The cylinder gas was introduced at increments of 0.2, 0.3, and 0.5 standard liters/minute, corresponding to 3.7, 5.0, and 9.4 ppmv H_2S in the syngas feed. Initial data suggested that hydrogen permeance was reduced by 40, 48, and 60 percent, respectively. However, within 30 minutes of stopping the H_2S flow, the membrane recovered its initial hydrogen permeance value. This rapid and complete recovery of hydrogen permeance following H_2S poisoning was unexpected but was confirmed by a repeat test with 9.4 ppmv H_2S.

5.4 Membrane Technology & Research Membranes

Membrane Technology & Research's (MTR's) 500 lb/hr CO_2 membrane system was tested in R10 for a total of 291 operating hours. This two stage membrane system with integrated refrigeration was designed to produce liquid CO_2 from syngas. Several issues encountered during this period prevented the skid from operating continuously throughout the run. They are listed below.

- The first-stage permeate compressor tripped several times on high discharge temperature as result of low cooling water flow. This was resolved by throttling a block valve to rebalance the flows between the supply and return lines.
- The chiller repeatedly tripped due to oil pump discharge pressure. MTR contacted the local representative for the chiller manufacturer. The equipment was inspected, and the pressure differential switch was adjusted, which appeared to resolve the issue.
- The nitrogen heater for dryer regeneration overheated and failed due to low nitrogen flow and was shipped back to the manufacturer for diagnosis and repair. This heater is essential for dryer bed operation. As a temporary work-around, the inlet syngas heater (used to prevent hydrocarbon condensation in the lines) was relocated and a spool piece installed in the vacant position.
- Membrane modules were replaced on three occasions due to system optimization and parametric studies.
- Water carryover from the hydrocarbon scrubber upstream of the MTR skid affected the membrane performance. The scrubber design will be reviewed and modified during the outage to minimize such carryover.

Despite the troubleshooting activities, the membrane system operated in an integrated manner and successfully demonstrated separation of CO_2 from syngas that was subsequently cooled and liquefied to produce high purity CO_2 product. The first-stage membrane produced a permeate stream containing 30 to 40 percent CO_2, similar to that produced by the 50 lb/hr membrane skid. The second stage membrane had high stage cut (fraction of feed gas that permeates the membrane) and ineffective pressure control due to an oversized back pressure regulator. As a result, the performance could not be reliably calculated. Nevertheless, liquid CO_2 was successfully produced at 30 bar, as evidenced from the liquid tank sight glass window, shown in Figure 4.

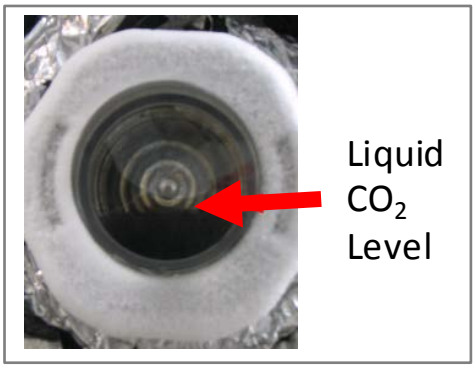

Figure 4. Sight Glass Showing Liquid CO_2 Level from MTR Membrane System.

A non-dispersive infrared analyzer indicated that CO_2 purity as high as 99 percent was achieved. Gas chromatography analysis identified the other gas compounds making up the balance, which are given in Figure 5.

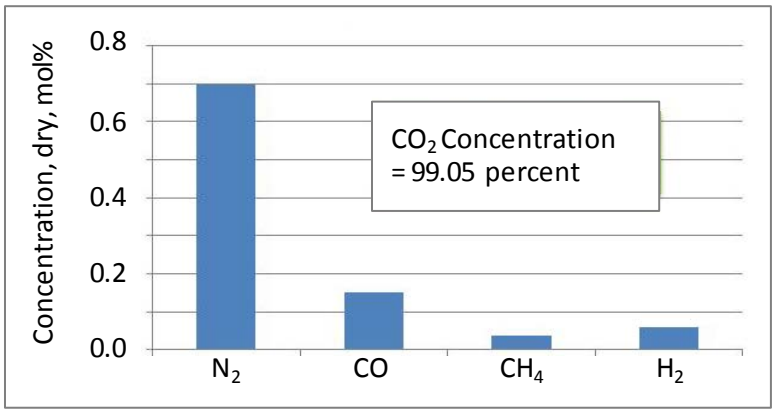

Figure 5. Balance of Constituents in CO_2 Product Stream from MTR Membrane.

Testing of the CO_2 membrane system will continue during R11, after resolving the issues identified in R10. Resolution of the issues included replacing several pressure gauges and flow meters, replacing the valve trim on a pressure regulator oversized for the flow, removing a check valve on the liquid CO_2 discharge line, and replacing a thermocouple on the nitrogen heater. MTR engineers will return to site prior to R11 to inspect the modifications, complete programmable logic controller changes, and oversee membrane module installation.

50 lb/hr CO_2 Membrane and Hydrogen Stamp Membrane

During R10, Polaris™ CO_2 membranes were tested at 50 lb/hr and Proteus™ hydrogen membranes at 1 lb/hr in support of continued membrane material development. One semi-commercial Polaris module, previously tested during R09, was tested during R10 for 670 hours, enriching CO_2 content fourfold, from about 10 percent in the feed to about 40 percent in the permeate streams. Separation performance remained stable over the two runs. Several Proteus membrane stamps were tested for a combined total of 582 hours, enriching hydrogen content from about 10 percent in the feed up to about 80 percent in the permeate while exhibiting

resistant to degradation from sulfur components. One Proteus material had hydrogen/H_2S selectivity of about 50, which reduces the sulfur content of the permeate and therefore reduces sulfur emissions.

MTR is in the process of converting their existing 50 lb/hr CO_2 membrane test skid to test hydrogen membranes. Hydrogen membrane materials have been tested in the 1 lb/hr stamp tester and laboratory-scale spiral-wound modules at 10 lb/hr. By scaling up to 50 lb/hr, more commercially represented modules can be used. The skid will need to be modified as CO_2 membranes operate at near ambient temperature while hydrogen membranes operate at around 300°F.

5.5 Media & Process Technology Membrane

During R10, Media & Process Technology (MPT) began to evaluate their full-scale water gas shift catalytic membrane reactor (CMR) based upon their carbon molecular sieve (CMS) membrane. Initially, MPT packed the WGS catalysts into their existing 86-tube membrane module to determine any potential damage to the membrane surface due to scratching by the catalyst or coking by the CO and hydrocarbons in the syngas. The annular space between the CMS membrane bundle and the housing plus the space between the tubes were packed with the WGS catalyst mixed with glass beads. Raw syngas containing about 8 percent moisture was fed (75 percent stoichiometric ratio of steam-to-CO) at the rate of 50 lb/hr to the reactor maintained at 210 psia and 500 to 570°F. No additional steam or hydrogen was added to the syngas. Under these conditions, approximately 25 percent of the CO was shifted to hydrogen. Throughout the test, the membrane flux remained stable, indicating minimal or no scratching or coking of the membrane surface. About 380 hours of running time was achieved during R10. At the end of the test, the bundle was returned to MPT for inspection and analysis.

Methane was present in the feed although it was not detected in either the permeate or the reject stream throughout the test. One possible mechanism for the methane removal is the decomposition of methane into carbon and hydrogen promoted by either the WGS catalyst or the CMS membrane. However, the decomposition reaction usually occurs above 1,380°F but not at the low membrane operating temperatures (500 to 570°F) used in the test. Attempts by MPT to duplicate these results in the laboratory using the synthetic stream were unsuccessful. However, chemical analysis of the samples of the catalyst used during R10 indicated the presence of 3.5 percent carbon compared to zero percent in the fresh catalyst. Further measurements will be made at the NCCC during the next runs.

In the beginning of R10, two of the CMS bundles installed suffered tube breakage possibly due to mechanical stress resulting from misalignment of the element during catalyst loading. This problem was overcome by adding a small gap in the catalyst bed at the top of the membrane bundle to relieve any catalyst stress on the membrane tubes. No failure due to tube breakage was noted in the subsequent tests conducted with the third bundle. Introducing the free space above the catalyst bed might have reduced or eliminated the stress exerted by the catalyst on the tubes.

In the next phase, MPT plans to enhance overall CO conversion by raising the catalyst dosage when the bulk of the glass beads is eliminated. In addition, up to 10 lb/hr of steam will be added to raise the steam-to-CO ratio to a value slightly above the stoichiometric amount.

5.6 Membrane Material Coupon Testing

Material testing efforts continued during R10 with a series of test coupons of metal alloys being investigated for hydrogen separation membranes. The coupons were placed in the PCD downstream of the filter elements where they were exposed to particulate free raw syngas in order to assess their resistance to degradation from syngas stream impurities, such as hydrogen sulfide. Following the run, the coupons were removed and sent to the suppliers for analysis.

5.7 TDA Research CO_2 Solvent

TDA Research's solid CO_2 sorbent system was tested for 384 hours during R10. About 3.5 lb/hr of sour, unshifted syngas was fed to the skid. TDA used its own WGS reactor, and the combined CO_2 sorbent and WGS catalyst to promote the WGS reaction. The test program goals were to assess the combined CO_2 separation and WGS performance over a range of WGS reactor operation. Combining the WGS reaction and CO_2 removal process in a single step drives the equilibrium-limited WGS reaction to increased hydrogen production without the need for large amounts of steam, thereby reducing the cost of CO_2 capture.

Test 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. Combining the WGS catalyst with the sorbent did not adversely affect its CO_2 capacity. At low steam-to-CO ratios, sorbent CO_2 capacity actually increased due to the lower partial pressure of steam.

5.8 University of Alabama CO_2 Capture Solvents

A series of tests were performed on solvents provided by the University of Alabama (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 R09 and R10 test campaigns. Solvents tested were 1-methylimidazole (MEI) and 1,2-dimethylimadizole (DMI).

The absorption of CO_2 from syngas as a function of time at 150 psig is shown in Figure 6. 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 6 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.

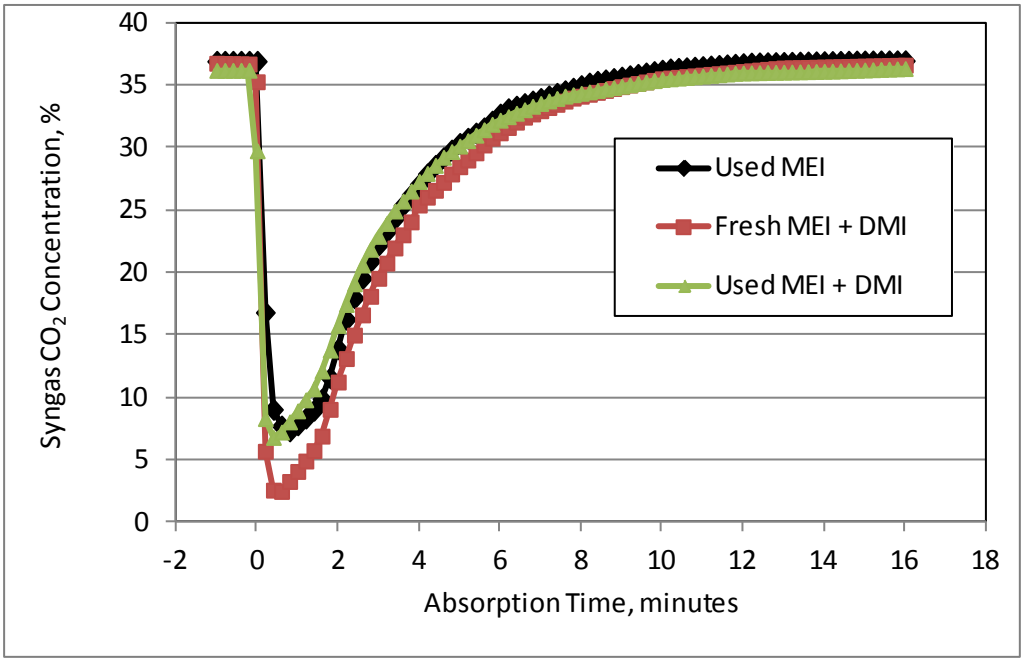

Figure 6. CO_2 Absorption versus Time for UA Solvents.

The total CO_2 capacity of the solvent is plotted as a function of CO_2 partial pressure in Figure 7. 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. The MEI fell in the range of the other solvents.

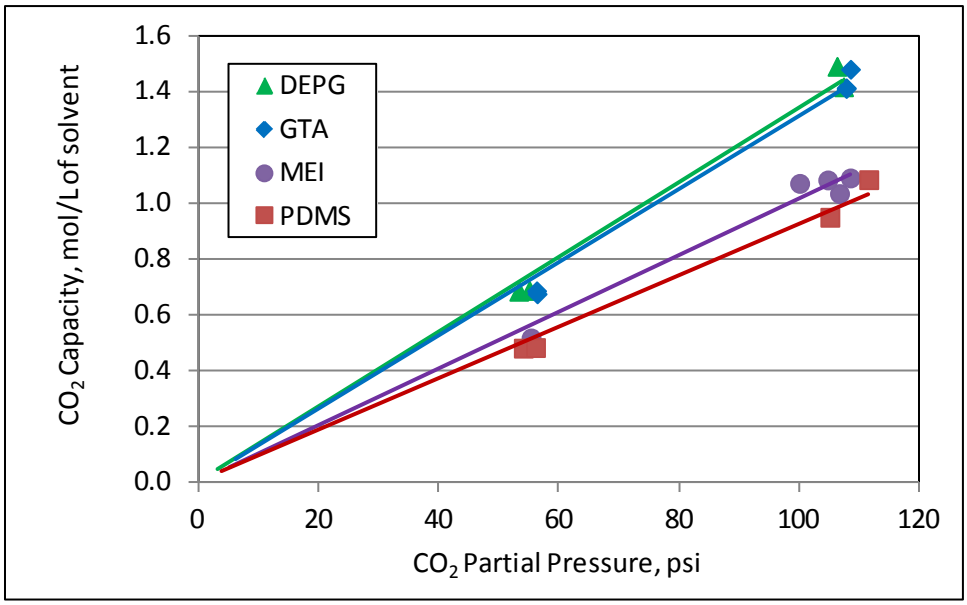

Figure 7. CO_2 Capacity of UA Solvent and Other Physical Solvents.

Figure 8 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.

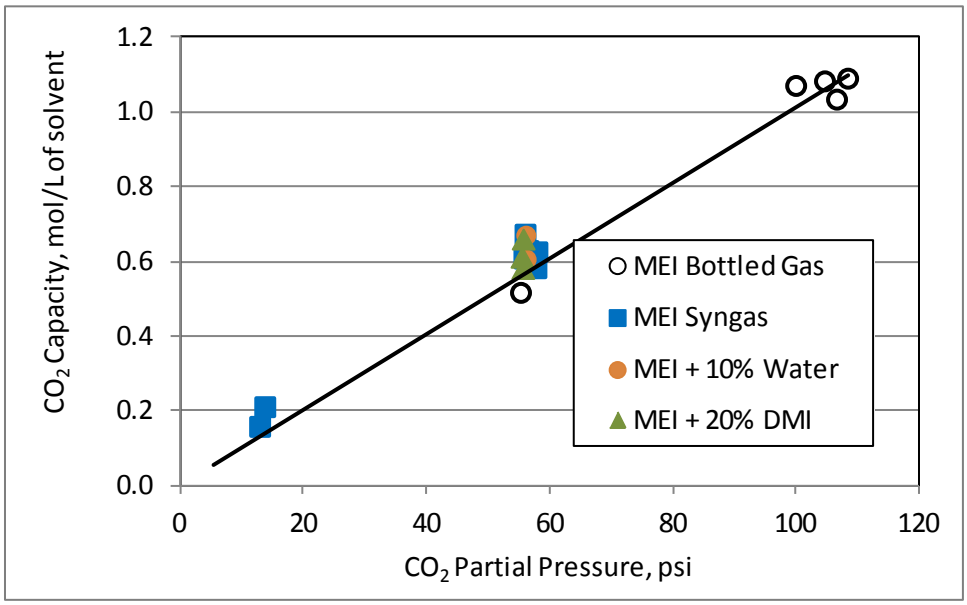

Figure 8. Comparison of Syngas and Bottled Gas Data for UA Solvent.

The outlet concentration of H_2S in the syngas during a number of absorption tests is plotted in Figure 9 and the H_2S capacity of each test is shown in Figure 10. Fresh solvent removed much more H_2S than did used solvent. This seems to be an irreversible reaction with some component of the solvent. Regeneration at temperatures up to 100°C did not remove this H_2S.

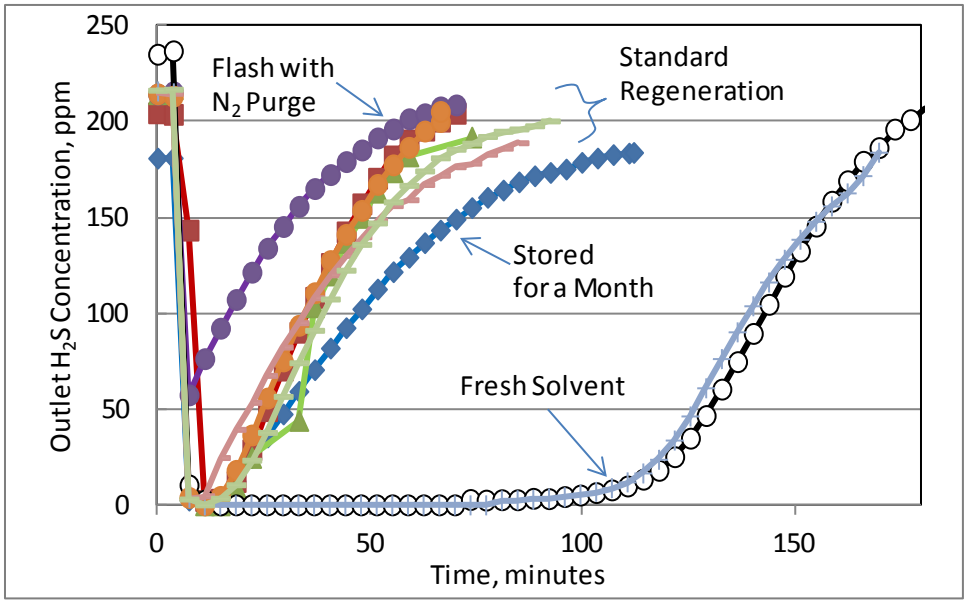

Figure 9. Absorption of H_2S from Syngas.

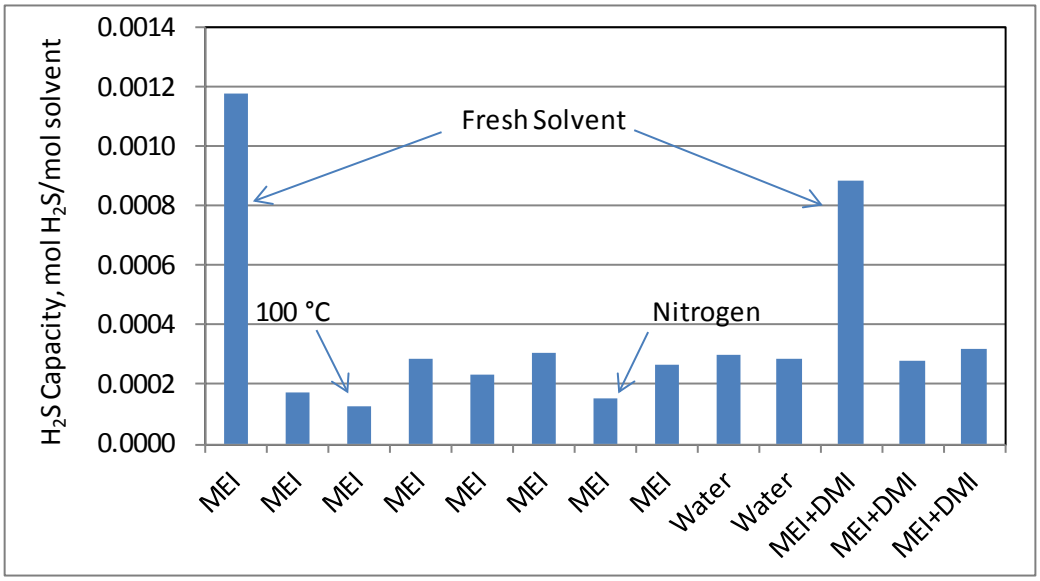

Figure 10. H_2S Capacity of Solvent with Syngas.

Flash regeneration was successful in removing a portion of the H_2S absorbed in a repeatable manner. Several different variations of the flash techniques were tried. For the curves in Figure 9 labeled "standard regeneration," the saturated solution was slowly depressurized while being stirred and maintained at absorption temperature. The reactor was then disassembled, the solution was poured into a container, weighed to determine if any was lost during the test, and then poured back into the reactor for the next test. Letting the solution sit in the container overnight rather than reusing it immediately did not appear to make a difference in the capacity.

However, letting the solution sit in the container for the months between R09 and R10 did seem to make a slight difference.

When the solution was regenerated by flashing then bubbling nitrogen slowly through the stirred solution at ambient pressure, the capacity was significantly less than for standard regeneration when the solution was poured back and forth in open air. Clearly, it needed more agitation and ventilation than was achieved with nitrogen purge in the reactor.

Some off-line tests are planned using bottled CO_2/nitrogen mixtures. Tests will be completed at 40°C to compare with the 20°C results, and the water content will be increased from 10 to 30 wt% to promote formation of bicarbonates and enhance CO_2 solubility.