NATIONAL CARBON CAPTURE CENTER
AT THE
POWER SYSTEMS DEVELOPMENT FACILITY

TEST RUN SUMMARY REPORT

TEST RUN R03
NOVEMBER 16, 2009 – DECEMBER 12, 2009

DOE Cooperative Agreement: DE-NT0000749

Recipient: Southern Company Services (SCS), Inc.
SCS Project Director: Kerry Bowers

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

February 2010

TABLE OF CONTENTS

Section ..... Page

List of Figures and Tables ii

List of Abbreviations iii

1.0 Executive Summary 1

2.0 Coal and Biomass Preparation 1

3.0 Coal Feeding 3

4.0 Transport Gasifier 4

5.0 Particulate Control Device 5

6.0 Ash Removal Systems 5

7.0 Advanced Syngas Cleanup 6

8.0 Gas Analysis 10

Appendix A Coal Characteristics 13

LIST OF FIGURES AND TABLES

Figure ..... Page

1 Wood Pellet Biomass Used as Gasification Feedstock in R03 2

2 PDAC Feed Line 3

3 Steady State Gasifier Operating Conditions 5

4 EDX Spectrum Obtained from Black Particles Filtered Out of Absorption Solution 7

5 Shift Conversion versus H2O-to-CO Molar Ratios for Fixed Bed WGS Testing 8

6 CO Conversion as a Function of Space Velocity for Filter Element WGS Testing 9

7 CO Conversion as a Function of Temperature for Filter Element WGS Testing 9

8 MTR Hydrogen and CO_2 Membrane Test Skid 10

9 Comparison of Syngas Moisture Measurements 11

Table ..... Page

1 Coal Properties before and after Milling 1

2 Biomass Properties before and after Milling 2

3 Steady State Carbon Conversion 4

4 Water-Gas Shift Test Operating Parameters 8

A-1 As-Fed PRB Coal Characteristics 13

LIST OF ABBREVIATIONS

CCAD—Continuous Coarse Ash Depressurization
CFAD— Continuous Fine Ash Depressurization
DOE—Department of Energy
EDX—Energy Dispersive X-Ray
FTIR—Fourier Transform Infrared
IC—Ion Chromatography
ICP/MS—Inductively Coupled Plasma/Mass Spectrometry
MMD—Mass Median Diameter
MPT—Media & Process Technology
MTR—Membrane Technology & Research
NFPA—National Fire and Protection Association
NCCC—National Carbon Capture Center
PCD—Particulate Control Device
PDAC—Pressure Decoupled Advanced Coal
PRB—Powder River Basin
PSDF—Power Systems Development Facility
R03—Run 3
SCS—Southern Company Services
SCU—Syngas Cleanup Unit
WGS—Water-Gas Shift

R03 SUMMARY REPORT

The DOE-sponsored National Carbon Capture Center (NCCC) at the Power Systems Development Facility (PSDF) has continued to support the advancement of clean coal technologies through testing under realistic industrial conditions. In November and December 2009, the PSDF operated its gasification process in test run R03, with the major objectives of testing of co-gasification of biomass and coal and testing of pre-combustion CO_2 capture technologies.

1.0 EXECUTIVE SUMMARY

Gasification test run R03 was planned for a nominal 500-hour duration during which the gasification process operated for the first time with biomass and coal co-feeding. R03 began on November 16 and ended on December 12, 2009, after 578 hours of gasification operation, including 200 hours of biomass co-feed. Operation with biomass co-feed commenced without significant feeder- or gasifier-related issues and yielded carbon conversions typically 99 percent or greater.

In addition to using biomass fuel, major objectives in R03 consisted of testing of pre-combustion CO_2 capture technologies. Other test objectives included:

- Optimizing operation of the developmental Pressure Decoupled Advanced Coal (PDAC) feeder
- Assessing the performance of various particulate control device (PCD) filter elements
- Testing of new gas analysis components
- Supporting testing of outside researchers in development of gas separation membranes

Operation of the gasification process during R03 allowed successful completion of all test objectives. The following sections highlight operation of the major equipment.

2.0 COAL AND BIOMASS PREPARATION

Powder River Basin (PRB) sub-bituminous coal and biomass (wood pellets) were processed in the mill system to reduce the moisture content and control the particle size distribution. Table 1 lists the average as-received and as-fed coal moisture and size data. As-fed coal composition characteristics are given in Table A-1.

Table 1.Coal Properties before and after Milling.

As-Received Moisture Content, wt %	30
As-Fed Moisture Content, wt %	23
Moisture Content Reduction, %	23
As-Fed Mass Median Diameter, micron	490
As-Fed Oversize (>1,180 micron) Content, wt %	20
As-Fed Fine (<45 micron) Content, wt %	11

The biomass used, shown in Figure 1, consisted of wood pellets supplied by Green Circle BioEnergy. The biomass was milled using one of the two existing roller mill systems.

Wood Pellet Biomass Milled Biomass

Figure 1. Wood Pellet Biomass Used as Gasification Feedstock in R03.

Table 2 lists the R03 biomass moisture and size data before and after milling. A few modifications were made to the mill operational settings for system air flow and pulverizer speed to effect the final particle size distribution. These changes were originally made during off-line milling of biomass in January 2009 and saved as a product recipe in the programmable logic controller system. Additionally, system pressure was decreased to raise air flow rates in order to improve material feed from the mill outlet cyclone collector to the pulverized silo. This change was necessary due to the difference in physical properties of biomass relative to coal. Overall the mill system operated well, processing a total of 105 tons of biomass for the run.

Table 2. Biomass Properties before and after Milling.

As-Received Moisture Content, wt %	7
As-Fed Moisture Content, wt %	4
Moisture Content Reduction, %	43
As-Fed Mass Median Diameter, micron	930
As-Fed Oversize (>1,180 micron) Content, wt %	38
As-Fed Fine (<45 micron) Content, wt %	11

While mill system operation was satisfactory, problems occurred with the dense phase pneumatic conveyor that transfers the processed biomass from the mill system pulverized storage silo to the coal feeder storage silo. The root cause of the transfer problems was a combination of flow restrictions in the discharge piping and insufficient conveying gas supply. First, the discharge piping layout was not conducive to the transfer of a lower density fibrous material such as biomass, as it contained several long radius elbows that reduced the velocity of the material enough to cause it to collect along the bottom of the piping, eventually forming a plug in the line. The fibrous structure of the biomass

allowed the individual particles to compress and interlock with one another, forcing them outward against the pipe wall and preventing the material from transferring. This occurrence had not been observed in previous operations when conveying coal from the pulverized silo to the feeder due to its non-compressible nature. The second and equally important cause for the transfer problem was that the system had an insufficient supply of conveying gas (nitrogen) to maintain conveying velocity of the biomass particles high enough to prevent line plugging.

Both of these problems were mitigated during the run by decreasing the amount of biomass charged to the conveyor and by re-arranging and adding conveying gas to the system. The discharge piping will be modified during the outage to remove excess elbows and other areas of unnecessary pressure drop. Additional conveying nitrogen will also be supplied to the system on a permanent basis in order to achieve the higher required line velocity for biomass transfer. While it is recognized that the dense phase conveying is not as well-suited for this application as other pneumatic conveying methods (i.e., dilute phase conveying with higher gas to solids ratios), the modifications suggested provide the most economical path to successful conveying of the biomass at this facility.

3.0 COAL FEEDING

Both the developmental and the original coal feeders operated without major feed stoppages. The PDAC feeder was used to feed coal only, and the original rotary feeder fed coal and then fed biomass during the co-gasification portion of the run.

Developmental Feeder. The PDAC feeder operated for 447 hours, including independent operations for 26 hours. The feeder operated at coal feed rates ranging from 760 to 4,400 lb/hr. Some plugging occurred due to the presence of large particles that accumulated in the oversize material trap in the PDAC feed line (see Figure 2).

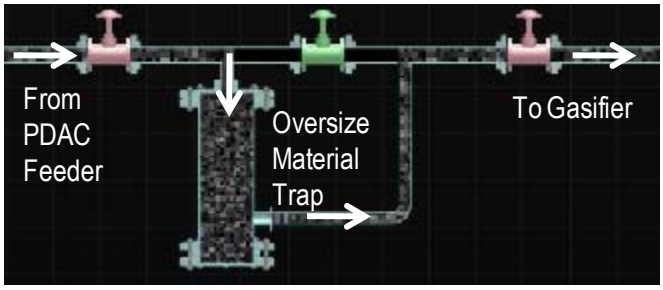

Figure 2. PDAC Feed Line.

Inspection of the large particles showed that they consisted mostly of agglomerated fines. In addition to PDAC feeder problems, coal preparation system operational problems were encountered during the run. Prior to shipment to the PSDF, the PRB coal had been pre-treated using a chemical and water mixture to suppress fugitive dust emissions, and this pre-treatment, which had not been employed before, may have exacerbated the coal handling problems.

Although the feeder experienced some problems during the run, several improvements in control logic were made. The lock vessel filling cycle was optimized using level probe indications. Vibration-type level probes, which were installed on the feeder dispense vessel and lock vessel prior to R02, reliably detected pulverized coal level in both vessels and proved a more reliable indication than the capacitance probes used previously. The vibration probes also do not require re-calibration in response to variations in feedstock bulk density. As a result of the increased reliability, the lock vessel filling cycle was optimized to use the level probe indication to end the fill cycle instead of waiting for the timer to time out. The benefit of this change is especially significant when operating the feeder at higher feed rates.

Further tuning was completed on the controller implemented during R02 to minimize the impact of lock vessel fill cycles on feed rate variability by maintaining a more constant dispense vessel pressure. Additionally, the instantaneous coal feed rate feedback control was tuned to further improve response to sudden changes in feed rate. Finally, a new control was created and implemented to control gasifier mixing zone temperature by varying the feed nitrogen and, thus, coal feed rate to the gasifier. This control was only tested for a short time at the end of the run and appeared to react well to temperatures changes, although additional tuning and optimization will be required in the future.

Original Coal Feeder. The original rotary coal feeder operated on-coal for 315 hours at feed rates varying from 1,500 to 2,650 lb/hr. The feeder was then transitioned to feed biomass only for 200 hours at feed rates from 450 to 1,000 lb/hr. The biomass feed rate accounted for an average of 22 weight percent of the total feed rate to the gasifier.

4.0 TRANSPORT GASIFIER

R03 operation consisted of 27 steady state operating periods. Gasifier operation during coal only feeding and during co-feeding of coal and biomass yielded high carbon conversions, as shown in Table 3.

Table 3. Steady State Carbon Conversion.

	Maximum	Minimum	Average
Coal Only Carbon Conversion, %	98.7	97.1	98.3
Biomass Co-Feed Carbon Conversion, %	99.6	98.9	99.2

Figure 3 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.

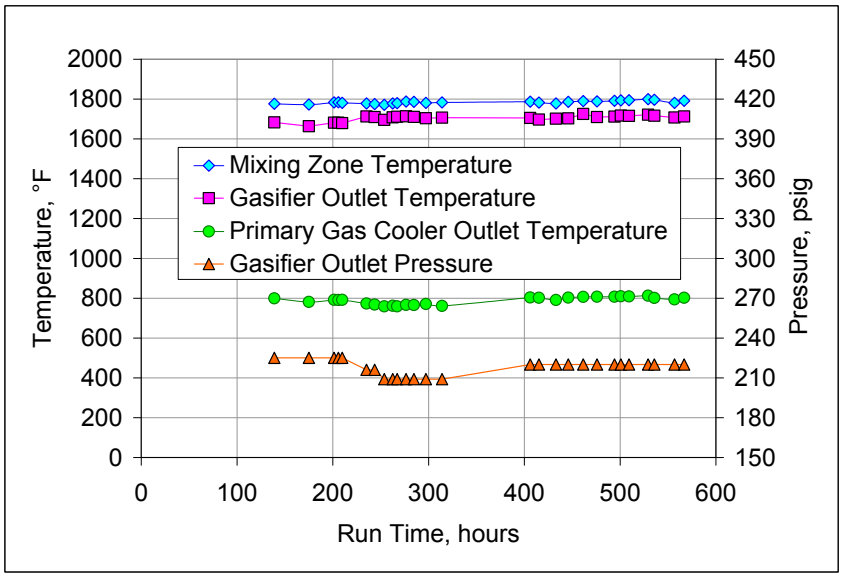

Figure 3. Steady State Gasifier Operating Conditions.

Gasifier Refractory. Inspections of the gasifier refractory showed that the hot-face refractory at the J-leg / standpipe intersection, which had been repaired prior to R02, was still in good condition. A slightly damaged area in the upper standpipe / solids separation unit intersection, which had been discovered prior to R01, continued to show acceptable condition. The damage noted appeared to be related to the extra stress that intersecting areas receive.

5.0 PARTICULATE CONTROL DEVICE

The PCD operated with high collection efficiency and stable pressure drop. PCD research continued to focus on material testing. The failsafes installed included Pall Dynalloy devices constructed of forward (supporting screen on the inner surface of the failsafe) and reverse structures (supporting screen on the outer surface), as well as PSDF-designed devices constructed of HR-160 material. The filter elements installed consisted of sintered fiber elements manufactured by Porvair, iron aluminide and HR-160 elements from Pall, and sintered powder filter elements with a high alloy material from Mott. The elements were left installed for further exposure in R04.

6.0 ASH REMOVAL SYSTEMS

Prior to R03, design and installation were completed for new piping and valves to bypass the original fine ash transport system consisting of a Clyde lock hopper rotary feeder. The new configuration represents a commercial system envisioned for ash removal from the Transport Gasifier, in which ash from the Continuous Fine Ash Depressurization (CFAD) system is discharged directly into an ash silo without intermediate transport equipment. The major advantages of bypassing the ash transport system include avoiding

the significant maintenance requirements of the lock hopper and reducing nitrogen costs (approximately $9,000 annual reduction at the NCCC).

The bypass line was operated for the majority of the R03 gasification run without observed problems, and inspections of several elbows following the run showed no evidence of line erosion. During R03, the reduction in nitrogen usage was not realized due to the addition of extra nitrogen to the ash silos. This nitrogen was added to comply with the National Fire and Protection Association (NFPA) 69 Standard on Explosion Prevention Systems, which was applied due to the possibility of a small amount of syngas in the transport gases and the lack of a direct measurement of oxygen concentration at the silos. The addition of extra nitrogen directly to the ash silos ensured compliance with the NFPA standard. Prior to R04, a new continuous oxygen analyzer will be added to the ash silos that will be interlocked to shut down the CFAD ash transport to the silo if oxygen concentrations greater than one percent by volume are detected. This installation will permit the additional nitrogen usage to be eliminated.

7.0 ADVANCED SYNGAS CLEANUP

CO_2 Capture Testing. The primary objective of the R03 testing was to gain better understanding of the co-capture of CO_2/H_2S. The ammonia solutions from the syngas absorption and regeneration tests were analyzed for metals and total sulfur content by inductively-coupled plasma/mass spectrometry (ICP/MS). The amounts of sulfur present in the form of sulfide and sulfate were also determined by titration and by ion chromatography (IC). The results confirmed the presence of iron, chromium, nickel, sulfide, and sulfate in both the absorption and regeneration solutions.

The ICP/MS analyses showed that significant amounts of sulfur remained in the solutions even after regeneration, suggesting that some of the sulfur was bound up in a heat-stable form. Potential heat-stable forms could include the sulfides of iron, chromium, and nickel. These metals were all found at levels sufficient to bind a significant portion of the absorbed sulfur. The presence of these metals may be associated with corrosion of stainless steel components and may explain some of the discoloration noted in the absorption solutions, since the sulfides of iron, nickel, and chromium are black. Figure 4 shows an energy-dispersive x-ray (EDX) spectrum obtained from the black particles that were filtered out of a discolored absorption solution.

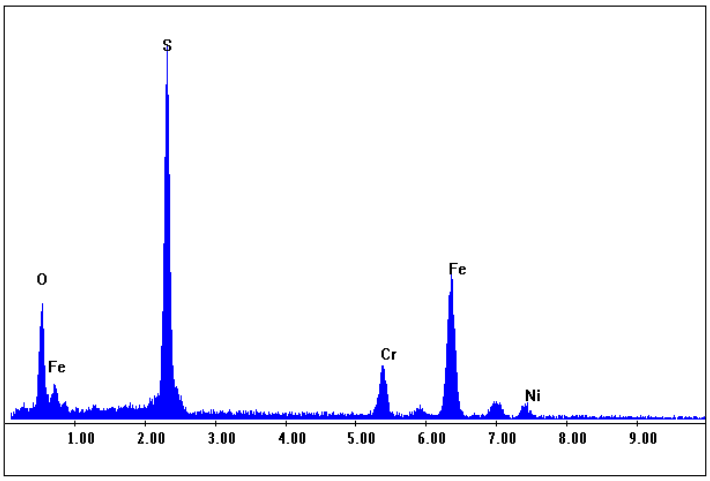

Figure 4. EDX Spectrum Obtained from Black Particles Filtered Out of Absorption Solution.

The presence of oxygen in the spectrum could be due to oxidation of the metal particles, or it could indicate the presence of oxygenated forms of metal-sulfur compounds such as sulfate, sulfite, bisulfate, or sulfamate. The IC analysis of the solutions suggested that some of the sulfur is present as sulfate; while the titrations suggested that some of the sulfur is present as sulfide. Moreover, comparison of the sulfide and sulfate analyses with the total sulfur determinations suggests that there may also be sulfur present in other forms. Analysis techniques are being investigated to determine in what other forms the sulfur may be present. The analytical data are being examined in detail to better understand these results.

In view of the possibility of forming heat-stable metal sulfides, the intentional addition of iron oxide was tested as a means of enhancing the capture of H_2S in aqueous ammonia. Two absorption/regeneration tests were completed with an initial iron oxide addition of 15 g in a total solution weight of 4.4 kg. This level of iron oxide was equivalent to about 3400 ppmw as iron oxide or about 2,400 ppmw as iron, which was about 5 times the highest iron concentration seen in previous tests. During the first absorption, the H_2S broke through at about the same time as the CO_2 and increased to a concentration of about 200 ppmv (the inlet H_2S was about 317 ppmv). The H_2S concentration then dropped again, leveling off at about 100 ppmv after 1.5 hrs of syngas absorption and remaining at that level for 2.5 hours after which the run was terminated. During the second absorption, using the regenerated solution from the first test, the CO_2 broke through after only a few minutes of absorption, but the H_2S remained at zero until the test was terminated after about an hour of operation. Data analysis is in progress to understand and explain these observations.

Water-Gas Shift Testing. Water-gas shift (WGS) testing with syngas took place in a fixed bed reactor and in catalytic filter elements in the syngas cleanup unit. Table 4 lists the operating parameters for the tests.

Table 4. Water-Gas Shift Test Operating Parameters.

	Fixed Bed Reactor	Filter Elements
Catalyst Size, micron	3 (Extrusions)	106 to 212
Pressure, psig	165	170
Temperature, ^{o}F	650 to 720	600 to 750°F
Syngas Flow Rate, lb/hr	40	33 to 55
Steam Flow Rate, lb/hr	0.3 to 1.4	0 to 4.5
Space Velocity, hr^{-1}	2,550 to 2,650	17,000 to 28,000
Face Velocity, ft/min	--	1.9 to 2.8

The fixed bed shift testing involved evaluation of shift conversion at varying H_2O-to-CO molar ratios. The results, plotted in Figure 5, were taken at a reactor inlet temperature of 650°F when no steam was added (corresponding to an H_2O-to-CO molar ratio of ~0.6) and for steam addition at rates from 0.2 to 1.4 lb/hr. The data indicated that acceptable CO conversions could be achieved at relatively low steam feed rates, which could provide significant capital and operating cost savings compared to high steam feed rate operation.

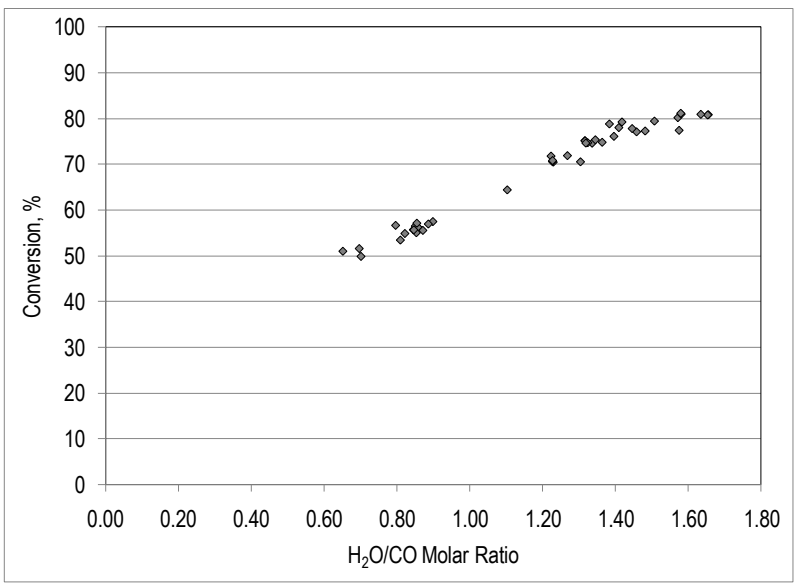

Figure 5. Shift Conversion versus H_2O-to-CO Molar Ratios for Fixed Bed WGS Testing.

For the catalytic elements, the CO conversion rate varied from 12 to 71 percent over a range of operating conditions. The test results shown in the following figures are based on average numbers in stable operating periods. Due to the limited number of test periods, the data points in each graph represent testing conditions with several varying parameters.

Figure 6 shows the CO conversion rate versus standard space velocity. As expected, the CO conversion rate increased as the standard space velocity decreased. It should be noted that the standard space velocity in the catalytic filter is roughly one order of magnitude higher than that in a typical fixed bed WGS reactor. Moderate CO

conversions can still be achieved at this high standard space velocity because the catalytic filter provides a near-perfect gas distribution in the catalytic layer.

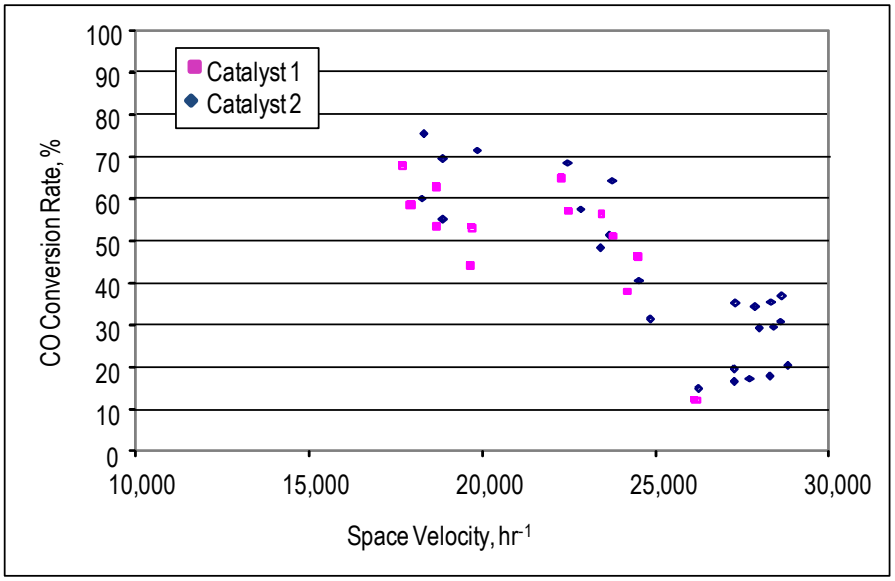

Figure 6. CO Conversion as a Function of Space Velocity for Filter Element WGS Testing.

The effect of inlet temperature on CO conversion is shown in Figure 7. As the inlet temperature increased, the CO conversion rate increased. Moderate CO conversion rates (about 30 to 75 percent) were achieved with inlet temperatures between 650°F and 750°F.

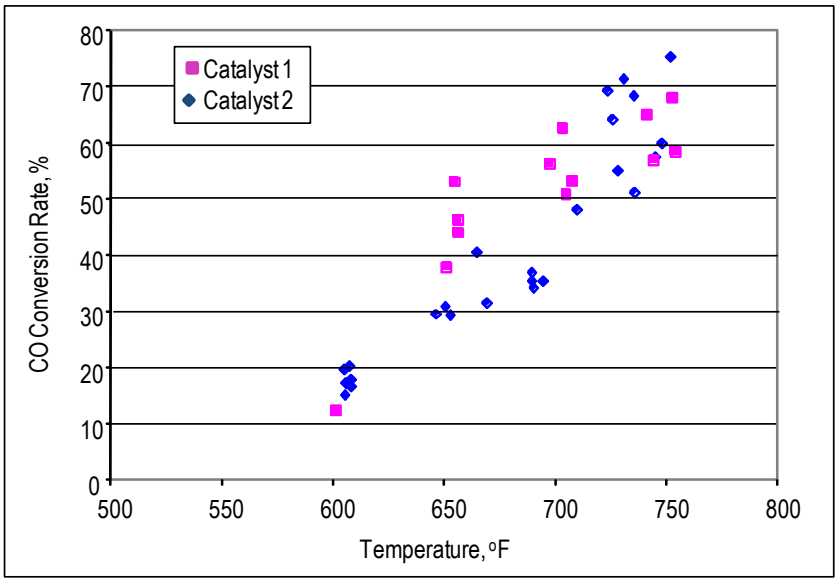

Figure 7. CO Conversion as a Function of Temperature for Filter Element WGS Testing.

Membrane Technology & Research (MTR) Hydrogen and CO_2 Membranes. During R03, MTR tested two types of membranes for the first time: one a low-temperature polymeric

material separating CO_2, and the other, a high-temperature membrane separating hydrogen. Both operated on syngas that was desulfurized. Figure 8 is a photograph of the MTR test skid.

Some modifications were required to the flow controls but in general the unit operated without any difficulties. The new syngas cooler and knock-out drum operated reliably, and gas analysis data upstream and downstream of the membrane were collected throughout the run.

Figure 8. MTR Hydrogen and CO_2 Membrane Test Skid.

The membranes proved easy to operate and were durable throughout 500 hours of operation. Preliminary data showed good performance of the membranes, and further analysis will be completed by MTR. Future testing is planned for R04.

Media & Process Technology (MPT) Hydrogen Membrane. The MPT hydrogen membrane, which has been tested at the PSDF since early 2008, was operated for about 100 hours. The test unit included 10 small hydrogen separation membranes, or carbon molecular sieves, connected in parallel and operating on raw syngas (without desulfurization treatment) at pressure.

A number of design and control issues were resolved early in the run, which involved fabricating a new pressure vessel to satisfy site safety requirements. Wiring changes were made to achieve fail-safe operation. During operation, bottled hydrogen was added to the syngas to raise the partial pressure of hydrogen close to that expected for a commercial plant. Data analysis is underway, and further testing is planned for R04.

8.0 GAS ANALYSIS

Dewcon Moisture Analyzer. Many analysis techniques have been employed at the PSDF for the measurement of water vapor in the syngas. The most accurate of the methods used are the condensation method from in-situ sampling (during PCD outlet particulate sampling

and an FTIR (Fourier Transform Infrared) measurement. Both of these techniques are reasonably accurate, but neither of them can provide continuous results. The condensation method is performed over several hours, resulting in an average moisture concentration for that time period. The FTIR technique gives instantaneous results, but due to contamination of the optical components, it can only be run for a short duration in a day. This produces a snapshot effect and is not useful for process monitoring.

The Dewcon moisture analyzer, first tested in R03, uses the dipole alignment of water molecules as the measurement technique. This makes the analyzer selective for water, and it is placed directly in the process stream, allowing for a very fast response time (less than 10 seconds). The probe provides continuous results which aid in calculating the efficiency of water-gas shift reactions. The Dewcon analyzer also showed quick response to system changes.

Comparisons of the three moisture measurement methods are presented in Figure 9. The data showed very good agreement (generally within 3.5 percent) between the Dewcon analyzer and the FTIR measurement.

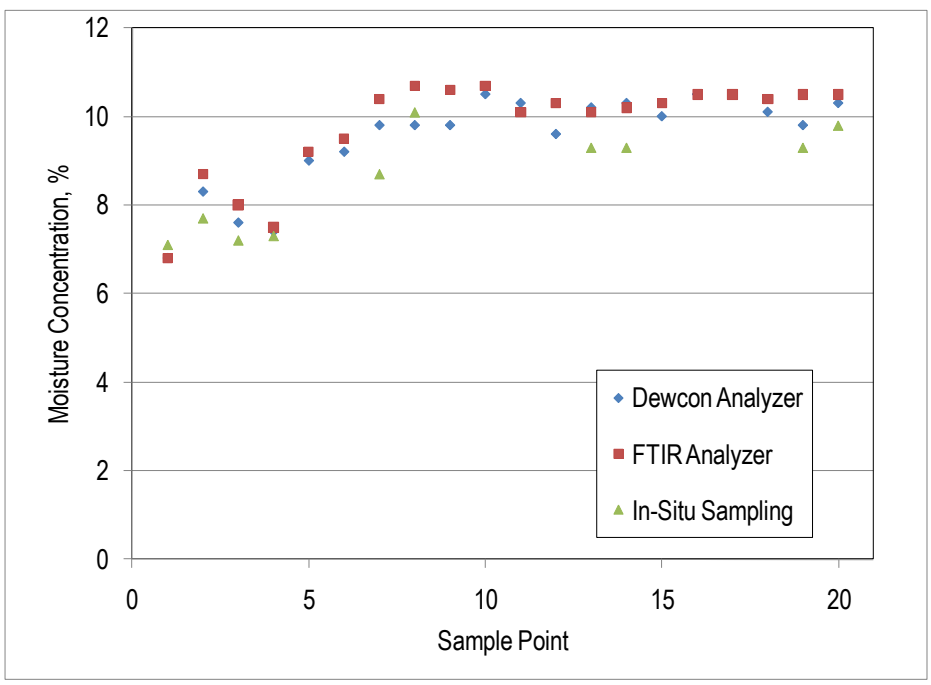

Figure 9. Comparison of Syngas Moisture Measurements.

Flue Gas Measurements. A new Rosemount XStream analyzer, in combination with a Permapure Nafion dryer, was installed prior to R03 at the outlet of the atmospheric syngas combustor. This system replaced an aging Procal in-situ analyzer. The Procal instrument used wavelength filtration and IR absorption to monitor several components simultaneously. This approach worked well for combustion processes, but the instrument had been in service for more than eight years, and the unit had become expensive to maintain (average $5K/test run). The Rosemount XStream is an extractive system, which

means the response time is slower than the Procal, but the XStream is easier to operate and much more stable. Maintenance costs should be much lower as well.

The PermaPure Nafion dryer removes the moisture from the flue gas without affecting the sulfur dioxide concentrations like standard condensing systems. The goal behind the purchase of the Nafion dryer was two-fold. First, a conditioning system for the syngas combustor was required, and second, this type of probe will be necessary for future applications at the planned NCCC post-combustion test facility. This provided the opportunity to field test the probe before purchasing others for the PC4 project. XStream/Permapure combination worked well, providing consistent and dependable results. Calibration of the instrument was not necessary during R03, but zero reading required adjustment on several occasions.

APPENDIX A COAL CHARACTERISTICS

The as-fed characteristics of the PRB coal used in R03 are listed in Table A-1.

Table A-1. As-Fed Coal Characteristics.

	Average	Minimum	Maximum	Standard Deviation
Moisture, wt %	22.7	22.2	23.1	0.35
Carbon, wt %	53.0	52.8	53.2	0.18
Hydrogen, wt %	3.4	3.4	3.5	0.06
Nitrogen, wt %	1.0	0.9	1.1	0.05
Oxygen, wt %	14.0	13.3	14.2	0.34
Sulfur, wt %	0.3	0.3	0.4	0.03
Ash, wt %	5.7	5.2	6.4	0.43
Volatiles, wt %	33.7	33.5	34.1	0.22
Fixed Carbon, wt %	37.9	37.7	38.1	0.18
Heating Value, As Received, Btu/lb	9202	9143	9276	53.6