The National Carbon Capture Center
at the Power Systems Development Facility

Test Run Summary Report

Gasification Test Run G-1
October 4, 2014 – November 6, 2014

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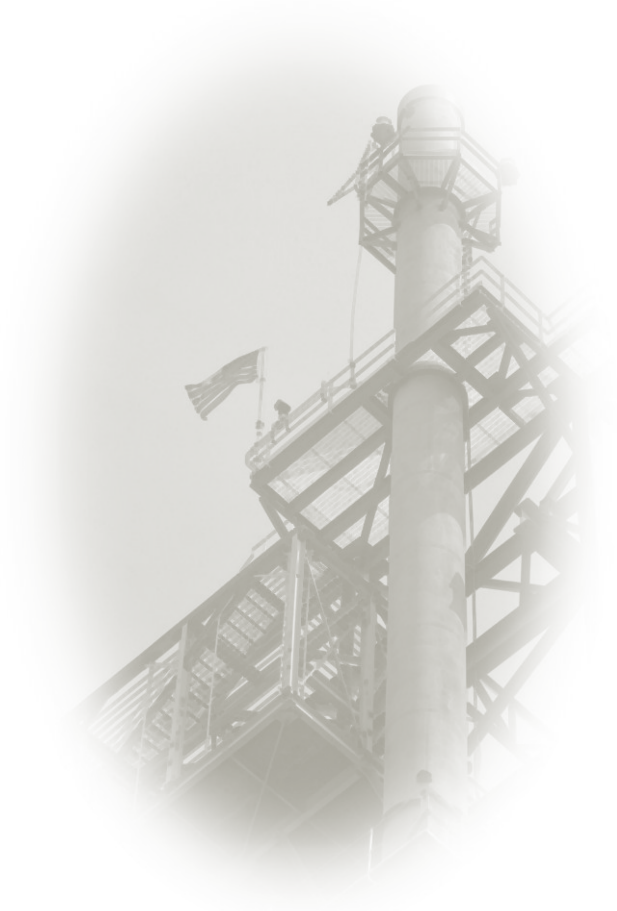

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List of Abbreviations

CMR	Catalytic Membrane Reactor
CMS	Carbon Molecular Sieve
COS	Carbonyl Sulfide
DOE	Department of Energy
F-T	Fischer Tropsch
G-1	Gasification Run 1
Gen-1	Generation 1
Gen-2	Generation 2
H_2S	Hydrogen Sulfide
MPT	Media & Process Technology
MTR	Membrane Technology & Research
NCCC	National Carbon Capture Center
PDAC	Pressure Decoupled Advanced Coal
PRB	Powder River Basin
PSA	Pressure-Swing Adsorption
R12	Gasification Run 12 (November 2013)
R13	Gasification Run 13 (March 2014)
SRI	Southern Research Institute
WGS	Water-Gas Shift

1.0 EXECUTIVE SUMMARY

The National Carbon Capture Center (NCCC) at the Power Systems Development Facility supports the Department of Energy (DOE) goal of promoting the United States' energy security through reliable, clean, and affordable energy produced from coal. As part of its mission to develop technologies for clean coal power generation, the NCCC routinely conducts testing of advanced gasification and CO_2 capture processes.

Gasification run G-1 began on October 4 and ended on November 6, 2014, with about 806 hours of operation achieved. The feedstock used during the run was Powder River Basin (PRB) subbituminous coal, with about 73 hours of the run comprising co-gasification with biomass at 20 wt% of the total feed rate. Less than an hour of interruption of gasification operation occurred throughout the run duration, and over 70 percent of the run consisted of steady-state periods. Steady-state carbon conversion averaged 98.4 percent during coal-only operation and averaged 99.1 percent during biomass co-feeding.

The run provided testing opportunity for a variety of developer technologies, as well as continued long-term evaluation of coal feeder instrumentation, gasifier refractory, and hot gas filter elements. Developer technology accomplishments of the G-1 run were:

- The first full syngas operation of the Southern Research Institute (SRI) Fischer-Tropsch (F-T) catalyst system, with effective system modifications based on initial operation in the previous run, and demonstrating stable operation and catalyst productivity more than four times greater than that of conventional F-T catalysts
- The first operation of a pressure-swing absorption (PSA) process from Air Products, with stable sorbent performance and system operation, good mass balance closures, 99.7 percent removal of hydrogen sulfide (H_2S) and more than 95 percent removal of CO_2 from syngas
- Continued operation of Johnson Matthey's mercury sorbent, demonstrating near complete mercury capture and long-term sorbent stability
- Continued operation of a water-gas shift (WGS) catalyst, allowing long-term evaluation of catalyst stability
- Testing of a carbonyl sulfide (COS) hydrolysis catalyst developed for high temperature operation
- Operation of the Media & Process Technology (MPT) Carbon Molecular Sieve (CMS) and combined operation with a palladium-based polishing membrane, demonstrating the ability to produce hydrogen with greater than 99 percent purity, and providing process data for further development of MPT's catalytic membrane reactor
- Testing of a hydrogen membrane module and stamp cells from Membrane Technology & Research (MTR) for continued high-temperature stability evaluations and material development

2.0 GASIFICATION TECHNOLOGIES

2.1 Coal Preparation and Feed

Table 1 lists the as-received and as-fed properties of the PRB coal used in G-1.

Table 1. Properties of PRB Coal Used in G-1

Coal Property	Average Value
As-Received Carbon, wt%	49.9
As-Received Hydrogen, wt%	3.3
As-Received Nitrogen, wt%	0.7
As-Received Sulfur, wt%	0.3
As-Received Ash, wt%	6.3
As-Received Oxygen, wt% (by difference)	11.6
As-Received Volatiles, wt%	30.6
As-Received Fixed C, wt%	35.2
As-Received Heating Value, Btu/lb	8,260
As-Received Moisture Concentration, wt%	28.0
As-Fed Moisture Concentration, wt%	18.9
Moisture Content Reduction, %	32.6
As-Fed Mass Median Diameter, microns	350
As-Fed Oversize (>1,180 microns) Content, wt%	6.9
As-Fed Fine (<45 microns) Content, wt%	11.2

Table 2 lists the properties of the biomass used for co-feed material during G-1. Since an air heater is not used to dry the biomass during milling as it is during coal milling, the as-fed values were equal to as-received values.

Table 2. Properties of Biomass Used in G-1

Biomass Property	Average Value
Carbon, wt%	47.8
Hydrogen, wt%	5.4
Nitrogen, wt%	0.3
Sulfur, wt%	0.3
Ash, wt%	0.9
Oxygen, wt% (by difference)	37.7
Volatiles, wt%	77.5
Fixed Carbon, wt%	13.9
Heating Value, Btu/lb	8,000
Moisture Concentration, wt%	7.7
Mass Median Diameter, microns	510
Oversize (>1,180 microns) Content, wt%	14.5
Fine (<45 microns) Content, wt%	2.7

The two coal feeders were operated throughout the run, with the original rotary coal feeder used for either coal or biomass, and the Pressure Decoupled Advanced Coal (PDAC) feeder used for coal only. The PDAC trim controller logic continued to operate consistently. As seen previously, the Densflow coal flow meter continued to show discrepancies with the coal feed rate as determined by the weigh cell. The Dynatrol vibration level probe installed in the lock vessel was replaced with a new probe of the same model prior to the run due to mechanical damage. The new probe performed reliably throughout the run. The Dynatrol probe in the dispense vessel also operated without incident. A secondary Drexelbrook capacitance point level probe in the dispense vessel was found to have failed after the run and will be repaired prior to the next run.

2.2 Transport Gasifier

The test run consisted of 59 steady-state periods lasting a total of 587 hours. Many of the steady-state periods were longer than 10 hours, with some longer than 24 hours. Steady-state carbon conversion for coal-only operation ranged from 97.5 to 99.9 percent and averaged 98.4 percent. Carbon conversion for the five steady-state periods achieved during biomass co-feed operation ranged from 98.6 to 99.3 percent, with an average value of 99.1 percent. Recycle syngas for gasifier aeration was used for 480 hours of the run. The newly installed primary gas cooler operated as designed and maintained an outlet temperature below 760°F throughout the run. Figure 1 plots the steady-state operating conditions of the gasifier.

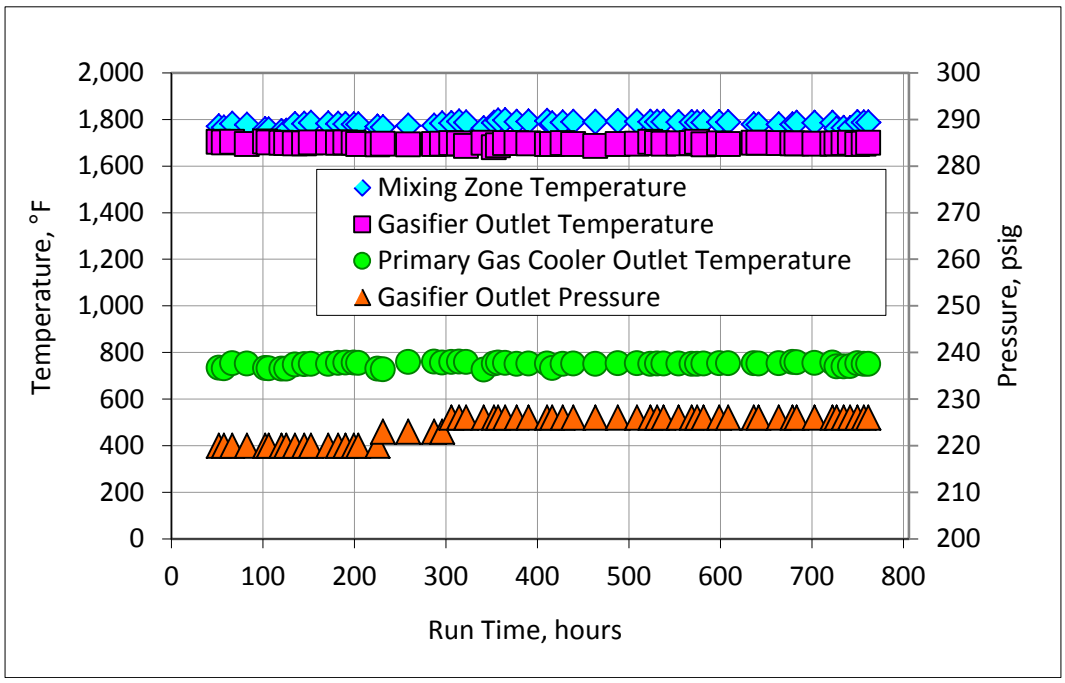

Figure 1. Steady State Operating Conditions

2.3 Gasifier Refractory Inspections

Inspections of the gasifier refractory were conducted following the run, and boroscope images from the inspections are provided in Figure 2. Areas of special interest included the seal leg return from the solids separation unit to the standpipe (shown in green in Figure 2), the J-leg/lower mixing zone interface (shown in red in the figure), and the J-leg/standpipe interface (shown in purple in the figure). A

comparison of boroscope images before and after G-1 indicates minimal wear in these areas, including the seal leg return area, which was repaired prior to the run.

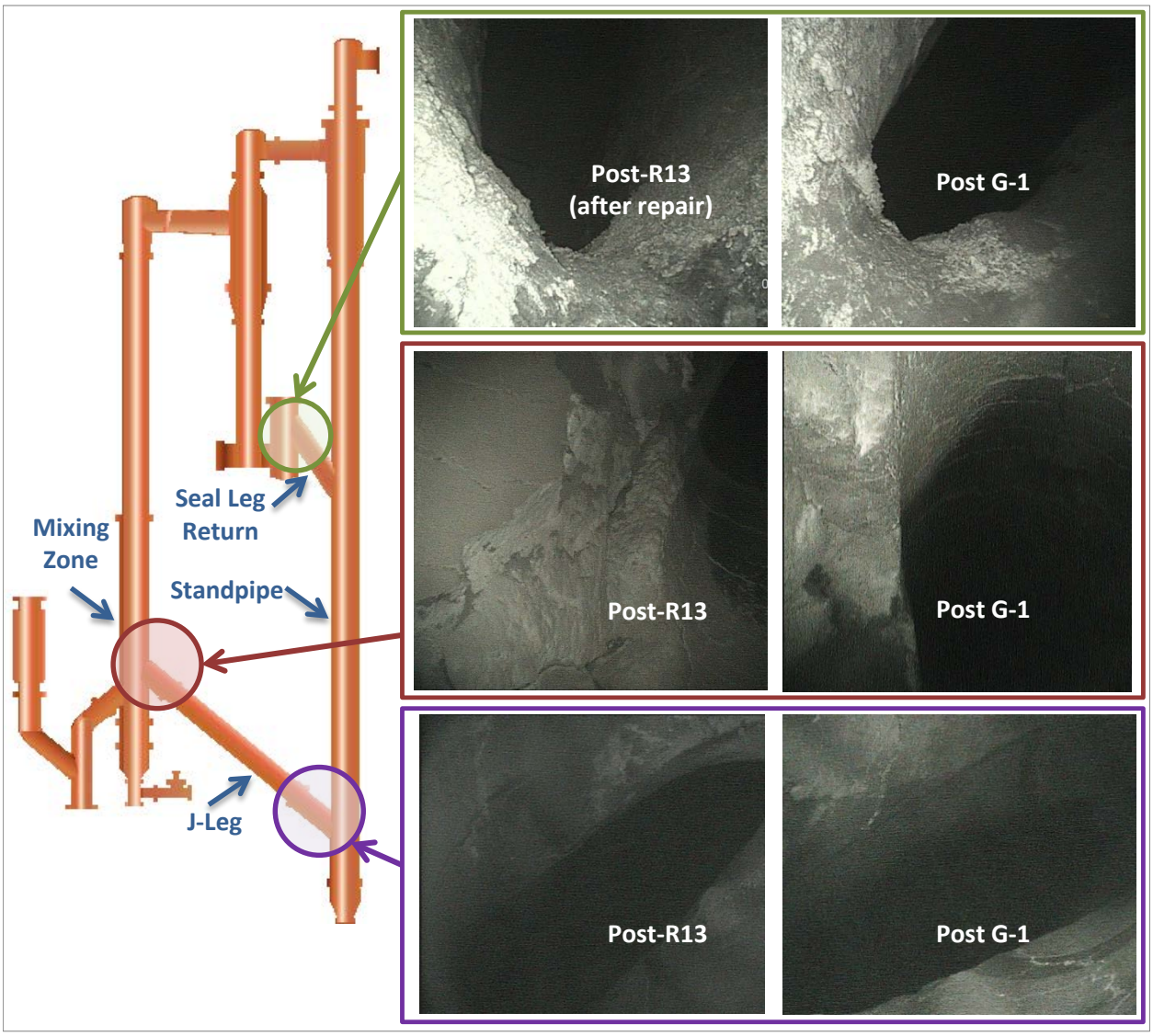

Figure 2. Schematic of NCCC Transport Gasifier with Refractory Inspection Images

One area which may require future repair was found at the bottom of the gasifier seal leg with an exposed anchor tip, which is shown in Figure 3.

Figure 3. Exposed Refractory Anchor in Gasifier Seal Leg

2.4 Particulate Control Device

The particulate control device operated with high collection efficiency and stable pressure drop. Although initial outlet particulate samples were contaminated with piping corrosion, subsequent sampling indicated outlet particulate loading below the sampling system detection limit of 0.1 ppmw. The filter elements, which are described in Table 3, will remain in place through the outage and the next test run.

Table 3. Hot Gas Filter Elements Tested during G-1

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

2.5 SRI Fischer-Tropsch Catalyst

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

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

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

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

2.6 Air Products Pressure-Swing Adsorption

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

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

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

The overall mass balance was within 1 percent, while component balances were within about 8 percent. The PSA rejected 99.7 percent of the H_2S and more than 95 percent of the CO_2 in the feed gas. Product gas purity was maintained at 1.4 ppm H_2S with a feed gas concentration of around 250 ppm. The

recovery of hydrogen to the product gas was 72 percent. Simulations are underway to compare the model predictions with these performance values.

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

2.7 Johnson Matthey Mercury Sorbent

The Johnson Matthey mercury sorbent was operated throughout the G-1 run with desulfurized, shifted syngas at a flow rate of 50 lb/hr with an operating pressure of 12.4 bar and a temperature of 260°C. NCCC gas analysis technicians took several inlet and outlet samples. No breakthrough of mercury, arsenic, or selenium was detected. The sorbent test duration was 556 hours, bringing the total testing of this material to over 4,000 hours distributed over 8 gasification runs.

2.8 Water-Gas Shift and COS Hydrolysis Catalysts

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

The COS hydrolysis catalyst tested was a newly developed honeycomb-shaped catalyst. The testing was conducted downstream of the developer's WGS catalyst. Gas analysis was run continuously at the vessel inlet and outlet. Table 4 provides the operating conditions for the hydrolysis catalyst and lists the average inlet and outlet COS concentration for each condition.

Table 4. Operating Conditions for G-1 Testing of COS Hydrolysis Catalyst

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

3.0 PRE-COMBUSTION CO_2 CAPTURE TECHNOLOGIES

3.1 Media & Process Technology Hydrogen Membranes

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

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

3.2 Membrane Technology & Research Membrane

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

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

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

Test Results for Four-Inch Proteus Membrane Module

A single four-inch Proteus membrane module was used for the entire run to measure membrane performance, long-term stability, and the effect of high-temperature syngas conditions on module components (spacers, glue lines, etc.). The skid temperature set point was 120°C for the duration of the run. Figure 4 shows the hydrogen concentration in the feed and permeate streams of the pilot-scale skid for the duration of run. The hydrogen concentration was enriched in the permeate to approximately three to four times the feed concentration, which is consistent with the previous Proteus module results from testing in 2014.

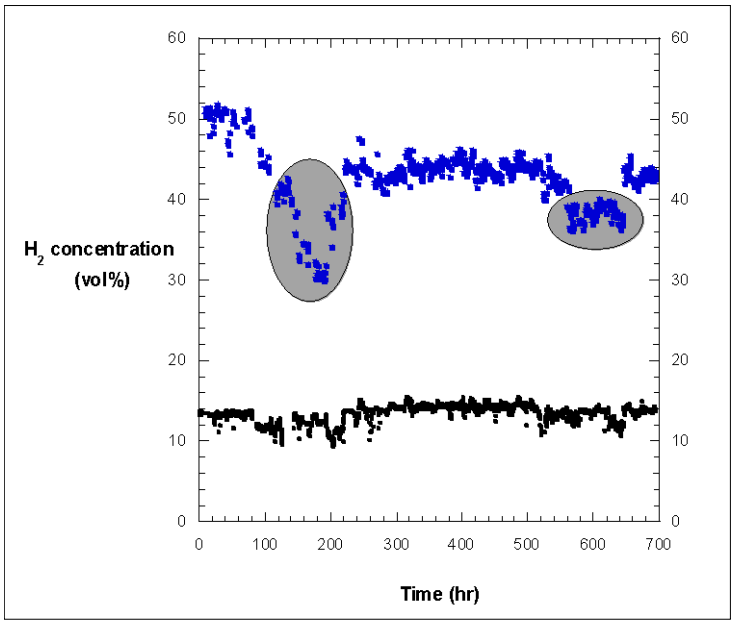

Figure 4. Hydrogen Concentration in the Feed and Permeate Streams of MTR Proteus Membrane Module during G-1

Some annealing or densification of the Proteus membrane is expected during the beginning of the campaign when the membrane module is first exposed to elevated temperatures. This is reflected in the reduction in the hydrogen permeate concentration during approximately the first 100 hours of testing. In the test time between approximately 120 hours and 240 hours (highlighted by the left gray oval in Figure 4), various operating parameters outside of the normal range led to reduced module performance. During this time, the skid was operating at a reduced flow rate (due to catalyst testing upstream of the MTR skid), which caused the skid to operate at a higher than ideal module stage-cut. For a portion of this time, the skid was also running at temperatures lower than 120°C, which led to reduced hydrogen permeance values. The final detrimental condition was plugging of the permeate orifice plate, which led to artificially high permeate pressures and therefore a reduced driving force for hydrogen permeation. The permeate orifice plate was also plugged between approximately 520 and 650 hours (as shown in the smaller, right gray oval in Figure 4), resulting in an appreciably lower hydrogen concentration in the permeate stream. When all operating parameters were within normal ranges, the permeate hydrogen concentration was consistently in the range of 40 to 45 vol% during the last 450 hours of testing.

Test Results for Gen-2 Proteus Membrane Stamps

First generation (Gen-1) Proteus membranes showed good hydrogen permeance and selectivity characteristics with syngas operation during previous NCCC runs. However, the inherent thermal stability of Gen-1 Proteus membranes restricts their operating temperature to less than 170°C. Since the outlet stream of a WGS reactor is typically about 200°C, it is desirable to have a membrane capable of operating at this temperature while still delivering hydrogen permeance and selectivity performance similar to Gen-1 Proteus.

Gen-2 bench-scale Proteus membranes were developed specifically for higher temperature operation. These newly developed membranes showed good stability and hydrogen separation characteristics at temperatures up to 200°C during MTR's preliminary lab testing. The first test of Gen-2 Proteus membranes under real syngas feed conditions was during run R13. Sulfur-containing syngas was fed to

two Gen-2 Proteus stamps operated in series for approximately 330 hours. Over that period, the temperature was varied from 118°C to 140°C, and the membrane stability and hydrogen separation performance were evaluated. Early shutdown of the R13 run prevented membrane performance at higher temperatures from being investigated.

The goal of the Gen-2 stamp tests during the G-1 run was to investigate separation performance and stability with sulfur-containing syngas at temperatures from 140°C to 200°C. The feed and permeate hydrogen concentrations during the stamp test are plotted in Figure 5. The hydrogen permeate concentration at 140°C (from 0 to 160 hours) was not consistent with that measured during R13 (80 to 85 vol%), and the concentration at 160°C was also lower than anticipated. A check valve that prevents back flow from the residue to the permeate was suspected to be faulty, resulting in low and highly fluctuating measurement of the permeate hydrogen concentration and permeate pressure. At approximately 300 hours, the permeate stream was isolated from the residue by closing a blocking valve and sending the entire permeate flow to the gas chromatograph. The measured permeate hydrogen concentration stabilized and was consistent with anticipated values after closing the blocking valve. The Gen-2 stamps showed good stability at 180°C and 194°C while still maintaining excellent hydrogen separation performance.

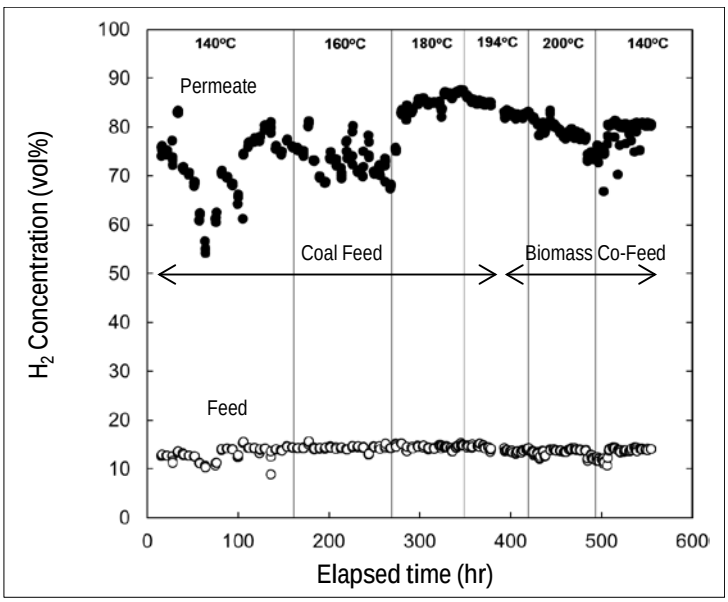

Figure 5. Hydrogen Concentration in the Feed and Permeate Streams of MTR Gen-2 Proteus Stamp Cell Unit during G-1

Table 5 summarizes the calculated average permeance and selectivity values for the Gen-2 Proteus membranes. Permeance and selectivity values for the first 270 hours were not included in this table because of the high degree of variance in permeate flow and composition measurements during that period. The best Gen-2 performance was measured at a feed temperature of 180°C, at which the hydrogen permeance and H_2/CO_2 selectivity were calculated to be 200 gpu and 22, respectively. After elevating the feed temperature to 194°C, the H_2/CO_2 selectivity was reduced to 19 while hydrogen permeance remained at 200 gpu. Relative to the values calculated at 180°C and 194°C, all gas permeance and H_2/gas selectivity values at 200°C were further reduced, suggesting that membrane densification and/or degradation occurred at the higher temperature.

Table 5. Average Permeance and Selectivity Values for the Gen-2 Proteus Stamps Tested in G-1

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

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