

**The National Carbon Capture Center
at the Power Systems Development Facility**

Test Run Summary Report

**Test Run R13
March 15, 2014 – April 14, 2014**

**DOE Cooperative Agreement
DE-NT0000749**



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List of Abbreviations

CH ₄	Methane
CO	Carbon Monoxide
COS	Carbonyl Sulfide
DOE	Department of Energy
FT	Fischer Tropsch
GC	Gas Chromatograph
MTR	Membrane Technology & Research
NCCC	National Carbon Capture Center
OSU	Ohio State University
PDAC	Pressure Decoupled Advanced Coal
PRB	Powder River Basin
R01 through R13	Test Runs 1 through 13
SCL	Syngas Chemical Looping
SRI	Southern Research Institute
TDL	Tunable Diode Laser
WGS	Water-Gas Shift
WPI	Worcester Polytechnic Institute

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 conducts testing of advanced gasification and CO₂ capture processes.

Gasification run R13 commenced from March 15 through April 14, 2014, for 836 hours of on-coal operation. The run was stable and demonstrated high carbon conversion while using Powder River Basin (PRB) coal as the feedstock. Gasification technologies tested in R13 included water-gas shift and COS hydrolysis catalysts, Johnson Matthey's high temperature mercury sorbent, the Ohio State University (OSU) Syngas Chemical Looping (SCL) process with start-up activities, Southern Research Institute's (SRI's) Fischer Tropsch (FT) catalyst, and the Tunable Diode Laser (TDL) from Stanford University. Test objectives involving pre-combustion CO₂ capture technologies consisted of operation of gas separation membranes from Worcester Polytechnic Institute (WPI) and Membrane Technology & Research (MTR).

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 R13.

Table 1. R13 PRB Coal Properties

Coal Property	Value
As-Received Carbon, wt%	49.88
As-Received Hydrogen, wt%	3.28
AS-Received Nitrogen, wt%	0.70
As-Received Sulfur, wt%	0.30
As-Received Ash, wt%	6.30
AS-Received Oxygen, wt% (by difference)	11.57
As-Received Volatiles, wt%	30.58
As-Received Fixed C, wt%	35.15
AS-Received Heating Value, Btu/lb	8264
As-Received Moisture Concentration, wt%	27.97
AS-Fed Moisture Concentration, wt%	21.54
Moisture Content Reduction, %	23
As-Fed Mass Median Diameter, microns	425
As-Fed Oversize (>1,180 microns) Content, wt%	13.6
As-Fed Fine (<45 microns) Content, wt%	6.2

Both the original rotary coal feeder and the Pressure Decoupled Advanced Coal (PDAC) feeder operated without major coal stoppages during R13. The original feeder operated for 835 hours at coal feed rates ranging from 952 to 2,560 lb/hr. The PDAC feeder operated for 792 hours at coal feed rates ranging from 2,024 to 3,175 lb/hr.

PDAC Logic and Instrumentation

The PDAC trim controller logic continued to maintain a consistent feed rate by adjusting nitrogen flow as necessary. 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 in the PDAC lock vessel did not function during the run, and post-run inspections revealed mechanical damage which impacted probe operation. A replacement-in-kind was ordered and it will be installed for the next test campaign. On-site maintenance personnel restored the damaged probe to working condition according to off-line shop testing, and the probe will be retained as a spare. The Dynatrol probe installed in the dispense vessel continued to operate without issue. The Drexelbrook point sensitive level probe installed in the dispense vessel that was changed prior to R12 due to an electrical failure performed well throughout the test campaign.

2.2 Transport Gasifier

Test run R13 included 67 steady state periods encompassing more than 722 hours with many steady state periods lasting more than 10 hours. The average steady state values of gasifier operating parameters are plotted in Figure 1.

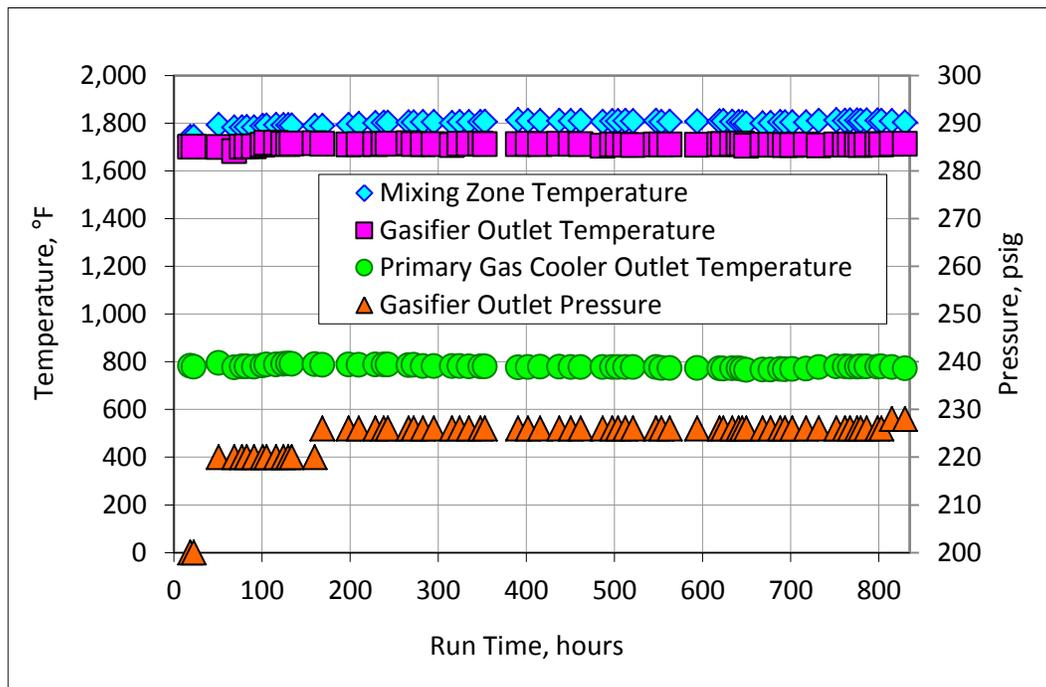


Figure 1. Steady State Operating Conditions

Steady state carbon conversion ranged from 98.7 to 99.6 percent, averaging 99.2 percent. The recycle gas compressor was not put in service during R13 due to vibration concerns. The gasifier temperature controller was used throughout the test campaign, and it maintained the outlet temperature within 7.5°F despite operating at a slightly lower than optimal coal feed.

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).

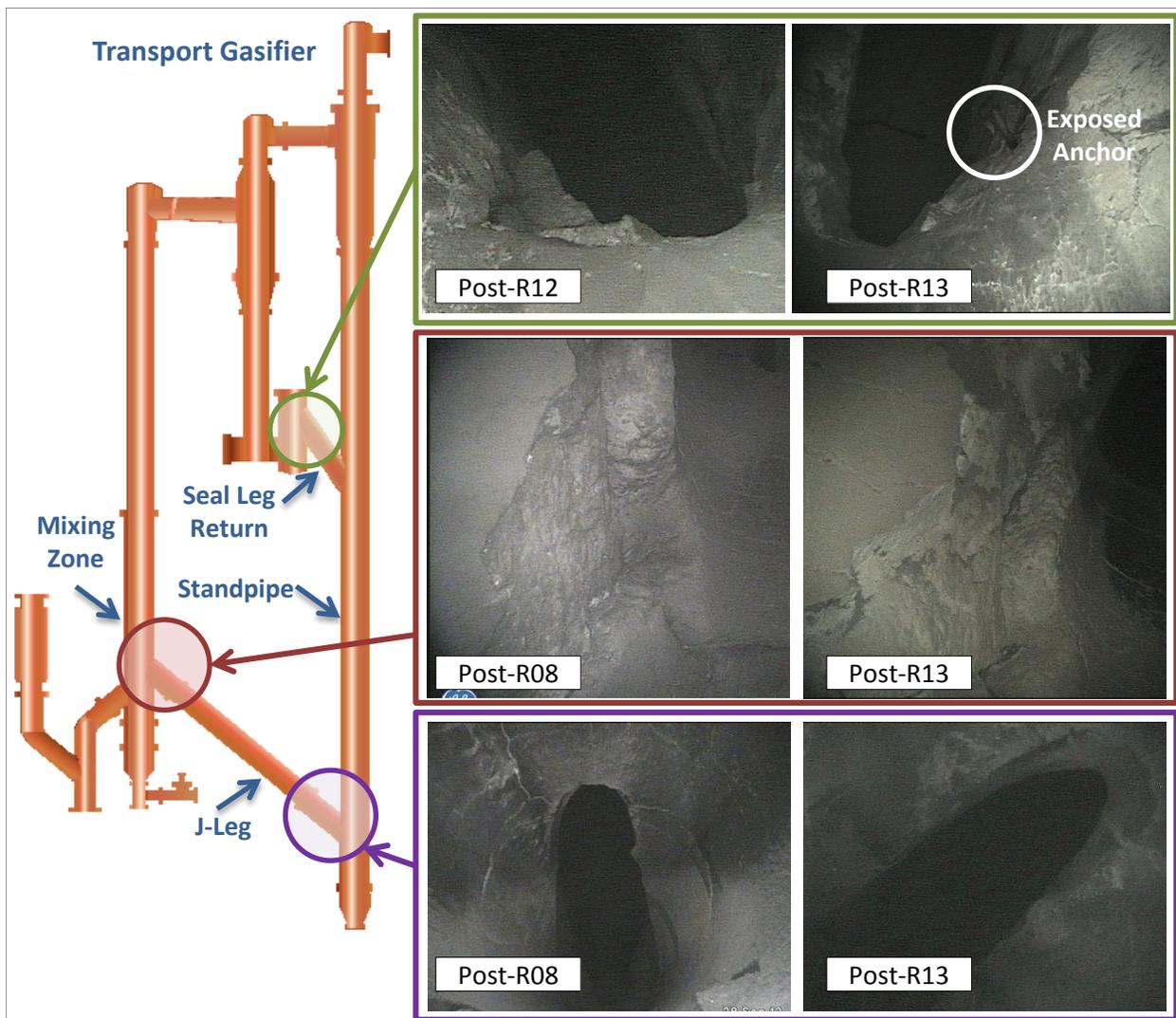


Figure 2. Schematic of NCCC Transport Gasifier with Refractory Inspection Images

One area of noticeably increased wear was the gasifier seal leg. While the seal leg return was in excellent condition overall, the seal leg itself showed new damage. The current condition is considered acceptable for continued operation, although the area will continue to be inspected following each gasification run to monitor the refractory wear. Both the J-leg/lower mixing zone interface and the J-leg/standpipe interface showed very little additional wear over the last several test campaigns.

2.3 Particulate Control Device

The particulate control device operated with high collection efficiency and stable pressure drop. All outlet sampling indicated outlet particulate loading below the sampling system detection limit of 0.1 ppmw. The filter elements will remain in place through the outage and the next test run.

2.4 Water-Gas Shift and COS Hydrolysis Catalysts

The developer's water-gas shift (WGS) and carbonyl sulfide (COS) hydrolysis catalysts that were tested in run R12 were tested further in R13, with each catalyst processing 50 lb/hr of syngas. Testing of the WGS catalyst consisted of 722 hours on syngas without any steam addition at an operating temperature of 400°F. This catalyst has been tested since R07 and has accumulated 3,517 hours of operation with no degradation of performance. The developer analyzed samples of the WGS catalyst and confirmed that there was no significant change in composition. The COS hydrolysis catalyst was operated at a range of temperatures from 480 to 640°F for about 550 hours, and showed the same conversion performance as that in R12. The developer plans to continue testing of the WGS catalyst and to test a new COS hydrolysis catalyst in the next run.

2.5 Johnson Matthey Mercury Sorbent

The Johnson Matthey high temperature mercury sorbent was tested at 500°F for 540 hours with 50 lb/hr of desulfurized syngas. Inlet and outlet gas samples taken during the run were sent to an outside laboratory for analysis. Table 2 lists the inlet concentrations of arsenic, selenium, and mercury. No measureable amount of breakthrough was detected.

Table 2. Inlet Concentrations of Metals during Mercury Sorbent Testing

	Arsenic µg/Nm ³	Selenium µg/Nm ³	Mercury µg/Nm ³
4/3/2014	0.14	3.68	10.47
4/10/2014	0.06	1.44	8.44
4/17/2014	0.04	0.82	5.41

2.6 Ohio State University Syngas Chemical Looping

OSU's SCL process uses countercurrent moving beds and iron-based composite oxygen carriers under reduction-oxidation conditions, converting coal-derived syngas into carbon-free energy carriers for electricity or hydrogen/chemical production. Initial commissioning of the SCL pilot unit at the NCCC began in 2013 and continued into 2014, with start-up beginning in run R13.

Start-up activities included process heater start-up, solids make-up and discharge sequence and operation check, and solids circulation studies under pressurized and heated operating conditions. Initial reactor heat-up was accomplished using electric heaters installed on the process gas supply lines. The reactor burner leg was test fired under a variety of reactor conditions. Continuous fire of the burner was not achieved, and the SCL team will incorporate design changes to resolve these issues.

The solids circulation studies were conducted at ambient pressure and pressures of 30, 60, and 132 psig. In each condition, solids circulation was confirmed using the system pressure balance and particle make-up system. The results indicated reliable reactor system operation with the expected syngas conversion capacity and hydrogen generation. Further, the results showed that the solid circulation rate is controllable within the full range of design conditions. Previous cold model studies at the Particulate Solid Research facility were performed under ambient pressure and temperature. The NCCC circulation studies were successfully performed at elevated and operating pressure for 184 hours without significant issues.

Multiple transient state operating conditions were simulated in preparation for the long-term unit operation. These simulated conditions trained the operations staff to:

- Maintain solid circulation while adjusting process temperature and pressure
- Recover from system trips safely
- Reinitiate solid circulation and pressurization
- Reinitiate process heater start-up and ramp up

2.7 SRI Fischer-Tropsch Catalyst

The SRI Fischer-Tropsch (FT) catalyst project aims to demonstrate a novel approach of FT synthesis that eliminates the conventional product upgrading and refining steps and enhances the ability of coal-to-liquids and coal/biomass-to-liquids processes to compete with petroleum-based processes. SRI's 5-lb/hr bench-scale test skid, shown in Figure 3, consists of a FT synthesis reactor system to produce liquid transportation fuels using a selective, wax-free, cobalt FT catalyst provided by Chevron.



Figure 3. Installed Southern Research Institute Fischer-Tropsch Skid

The first test campaign of this system at the NCCC was conducted during R13 and included system commissioning, catalyst testing with bottle gas, and syngas cleanup testing. Catalyst testing with syngas was not completed due to operational issues. The major accomplishments of the testing are listed below.

- Successfully activated the FT catalyst using pure hydrogen
- Operated the unit for over 60 hours using bottled syngas
- Maintained a hydrogen-to-CO ratio of 1.95 to 2.01 during the bottled gas testing
- Achieved designed conversions and production rates of more than 2 liter/day
- Demonstrated high catalyst hydrocarbon productivity of 0.65 to 0.75 gram (as carbon) per gram of catalyst/hr at 225°C with 34 percent hydrogen, 17 percent CO, and 49 percent nitrogen
- Successfully operated pumpless thermal siphon heat removal system
- Demonstrated efficient heat removal and nearly isothermal conditions in the two-inch fixed-bed reactor (All previous bench- to pilot-scale studies by others in the field have been limited to a one-inch or less diameter reactor and have not achieved isothermal operation. This was considered by Chevron as the most significant achievement as previous attempts have failed.)
- Successfully ran raw syngas at inlet pressure (175 to 190 psig) and temperature (450 to 600°F) for over 24 hours
- With syngas feed, verified that tar (particularly naphthalene) does not cause any plugging prior to the tar trap
- Verified syngas compressor operation

The NCCC designed and installed an additional bottle gas delivery system, shown in Figure 4, prior to the run to support the SRI catalyst testing. A tube trailer was sited to supply the needed amounts of hydrogen, and additional fixed fire protection equipment and a code compliant fire barrier system were installed.



Figure 4. Hydrogen and CO Bottle Gas Supply System with Fire Barrier

2.8 Stanford University Tunable Diode Laser

Under DOE sponsorship, Stanford University has been developing the Tunable Diode Laser, a prototype in-situ laser-absorption sensor for the real-time syngas composition measurements. For R13, the TDL, which was first tested at the NCCC in 2012, was modified to monitor syngas carbon monoxide (CO) and methane (CH₄) concentrations in addition to steam concentration and temperature.

Time-resolved concentration data from all four species, CO, CH₄, CO₂, and H₂O, were successfully collected from the beginning of the test run, as shown in Figure 5. This data shows the transition from combustion-mode operation for gasifier heat up to gasification mode at around 114.3 hours. During the gasifier start-up, the laser transmission was attenuated by more than 99.9 percent by the scattering from particulate in the syngas. Even at the low laser transmission conditions, the sensor was able to simultaneously monitor all four species with sub-second time resolution with signal-to-noise ratios better than 10 on all four species. Note the sharp rise in CO and CH₄ concentration near 114.3 hours in Figure 5 indicates the onset of gasification.

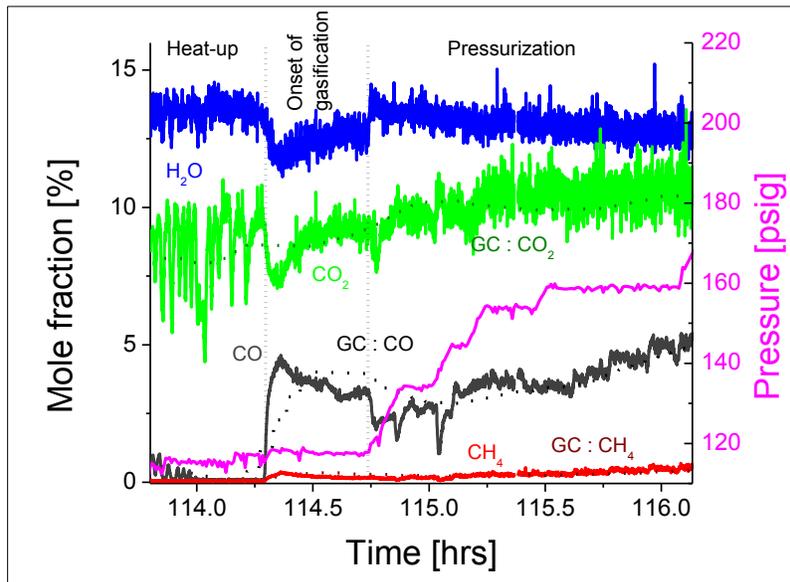


Figure 5. TDL and GC Measurements of Syngas Composition during R13 Start-Up

The figure also illustrates the advantage of the rapid time response of the laser absorption sensor compared to the Gas Chromatograph (GC) analysis of sampled syngas. Although the mole fractions of the GC and the laser absorption are in good agreement, the GC data was shifted by 20 minutes due to the time delay of flow between sample point and GC measurement. The large volume of the sampling gas filtration and drying also degrades the GC time-response to show a 12.5 minute rise time as is evident in the CO measurements by the GC compared to the CO laser measurement. H₂O and CO₂ are present in the syngas from both combustion and gasification, and at the onset of gasification their mole fraction declines. The rapid fluctuation in their mole fractions follows the batch coal feeder and is thought to be real temporal dynamics in the syngas composition and not sensor noise.

The GC data showed steady syngas composition after 121.7 hours as illustrated in the data in Figure 6; however, the laser absorption sensor showed there were temporal fluctuations on the time scale of the coal batch feed, and the CO and CH₄ showed a slower variation with a period of approximately 30 minutes.

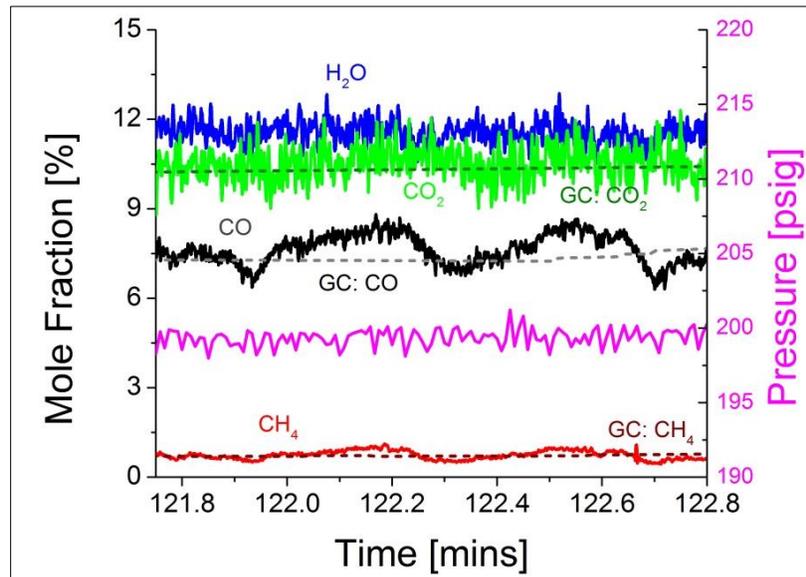


Figure 6. TDL and GC Syngas Composition Measurements during Steady State Gasifier Operation

The slow oscillations in the CO and CH₄ mole fractions in Figure 6 eventually dampened out after more run time as illustrated in Figure 7 for data near 930 hours. In addition, both the CO and CH₄ mole fractions became significantly larger than those near start-up. While the average values of CO, CO₂, CH₄, and H₂O were quite steady, the mole fractions continued to track the gasifier temperature with a time constant equal to the coal batch feed rate. Concentrations of CO₂ and H₂O showed a positive correlation with temperature, and concentrations CO and CH₄ showed a negative correlation.

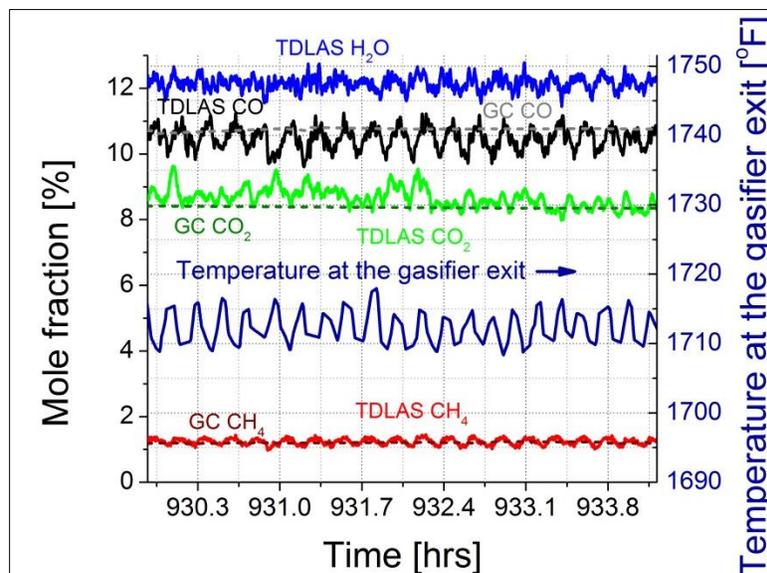


Figure 7. TDL and GC Syngas Measurements after 930 Hours

The test results suggest that the sensor could be used for gasifier control. This work resulted in five significant advancements for laser absorption sensors for practical combustion and gasification applications:

- A novel fiber bundle was developed to combine multiple extended near infrared laser-beams onto a single optical path.
- A normalized, wavelength-scanned wavelength modulation spectroscopy strategy was used for species measurements in dusty syngas with more than 99.9 percent laser transmission losses due to scattering.
- The sensor strategy allowed for sub-second time resolution for simultaneous measurements of four species.
- The prototype sensor demonstrated remotely adjustable detector gain and beam adjustment that enabled alignment optimization that met the safety requirements needed for operation with syngas.
- The optical engineering was sufficiently robust to enable operation without further operator intervention over the entire 54-day measurement campaign.

3.0 PRE-COMBUSTION CO₂ CAPTURE TECHNOLOGIES

3.1 Worcester Polytechnic Institute Membrane

WPI tested a palladium alloy hydrogen membrane during R13. The membrane has a proprietary surface coating from T3 Scientific to protect the membrane from trace containments in syngas. Testing began on March 20 using 10 lb/hr nitrogen with hydrogen to establish baseline performance. The feed gas was then transitioned to shifted, sweet syngas with hydrogen enrichment to obtain 38 vol% hydrogen in the feed gas. Testing concluded on April 18, for a total of 721 hours with 528 hours on syngas with hydrogen enrichment.

Figure 8 shows the permeance over time during R13. During the initial operation with nitrogen/hydrogen gas, the hydrogen permeance slightly increased to 7.3 scfh/ft²/psi^{0.5} before syngas was introduced. This corresponded to a 55 percent decrease in the hydrogen permeance compared to the permeance measured at WPI's lab. After syngas was introduced, hydrogen permeance continued to increase gradually to about 10 scfh/ft²/psi^{0.5}, and then eventually stabilized at around 9 scfh/ft²/psi^{0.5} until the end of the test. Product hydrogen purity was above 99 percent throughout the test period. The membrane will be subjected to standard permeation and recoverability testing in a pure hydrogen atmosphere at the WPI lab.

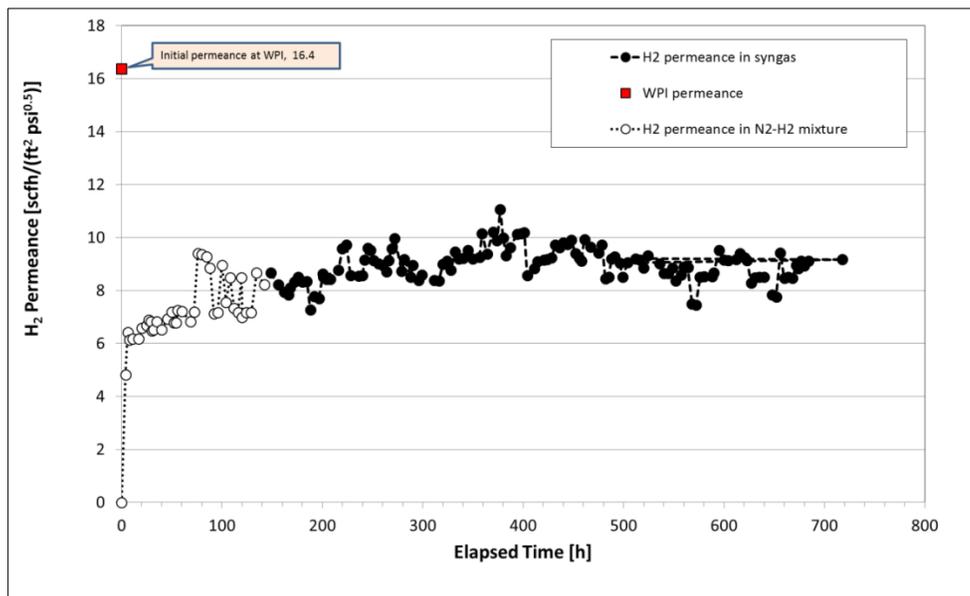


Figure 8. Hydrogen Permeance Profile of WPI Membrane Tested during R13

3.2 Membrane Technology & Research Membrane

50 lb/hr Hydrogen Membrane

MTR tested a single four-inch Proteus hydrogen membrane module during R13 beginning on March 19. The test objectives were to evaluate membrane performance, long-term stability, and the effect of high-temperature syngas conditions on the module components (spacers, glue lines, etc.). The membrane treated 50 lb/hr of sour, shifted syngas. Operation of the module was initially conducted at 200°F and then gradually increased in 25-degree increments until it reached 300°F to collect performance data at each temperature.

The hydrogen content of the feed syngas and permeate gas streams during the 529 hours of operation are plotted in Figure 9. During the first 100 hours, as shown in the figure, the permeate hydrogen concentration varied with the fluctuations of feed hydrogen concentration, indicating that the module was leak-free and of high quality. While enrichment of hydrogen in the permeate stream was consistently four times the feed concentration, the values were lower than expected. In addition, the membrane performance was found to be less sensitive to the system temperature than were stamp cells previously tested. The membrane module was returned to MTR for post-test analysis.

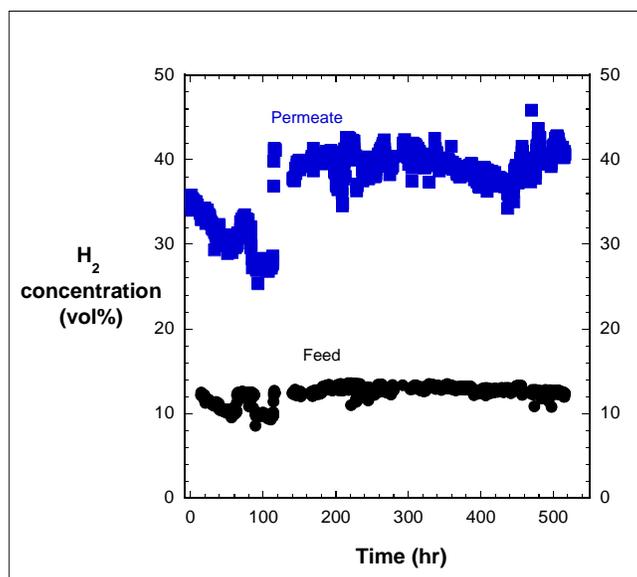


Figure 9. Hydrogen Concentration in Feed and Permeate Streams of the MTR Hydrogen Membrane

CO₂ and Hydrogen Stamp Cells

In addition to the hydrogen membrane module test, MTR tested various advanced membrane materials for CO₂ and hydrogen separation using small stamp cells. Two CO₂-selective stamp cells and one higher temperature hydrogen stamp cell were tested.

The two new CO₂-selective membranes showed improved selectivity in laboratory pure-gas and mixed-gas experiments. The CO₂ permeance and selectivity values of the membranes tested in stamp form using syngas feed during R13 are given in Table 3. While the lower CO₂ permeance of the membranes was expected, the selectivities were not a major improvement (and were lower in some cases) when compared to that of current baseline Polaris CO₂ membrane performance values under similar conditions. The cause for the unexpectedly low selectivities is under investigation.

Table 3. Permeance and Selectivity Values of CO₂-Selective Membrane Stamp Cells Tested during R13

Membrane	CO ₂ Permeance, gpu	Selectivity		
		CO ₂ /N ₂	CO ₂ /CO	CO ₂ /H ₂
Membrane A	110	32	23	7.1
Membrane B	210	19	12	3.8

First generation (Gen-1) Proteus hydrogen membranes that have been tested at NCCC showed good hydrogen permeance and selectivity characteristics. However, the inherent thermal stability of Gen-1 Proteus membranes restricts their operating temperature to less than 392°F. Since the outlet stream of a low temperature WGS reactor is typically about 392°F, it is desirable to have a membrane capable of operating at this temperature while still delivering hydrogen permeance and selectivity performances similar to that of the Gen-1 Proteus.

Second generation (Gen-2) bench-scale Proteus membranes were developed specifically for higher temperature operation (i.e., 302 to 392°F). These newly developed membranes showed good stability and hydrogen separation characteristics up to 392°F during MTR's preliminary lab testing. The first test of Gen-2 Proteus membranes under syngas feed conditions was conducted during R13. Sulfur-containing syngas was fed to Gen-2 Proteus stamp for approximately 330 hours. Over that time, the temperature was varied from 244°F to 284°F, and the membrane stability and hydrogen separation performance were evaluated. However, higher temperature testing was not carried out due to problems with a water circulation pump on the syngas condensing tank upstream of the skid.

The feed and permeate hydrogen concentrations during the stamp cell test are summarized in Figure 10. In addition to showing excellent stability over the duration of the run, the Gen-2 membrane hydrogen separation performance was very good at each of the three temperatures evaluated. The hydrogen was enriched from 12-percent in the feed to approximately 83 to 86 percent in the permeate. Overall, Gen-2 Proteus membrane performance was very similar to or slightly improved over that of the Gen-1 Proteus stamps.

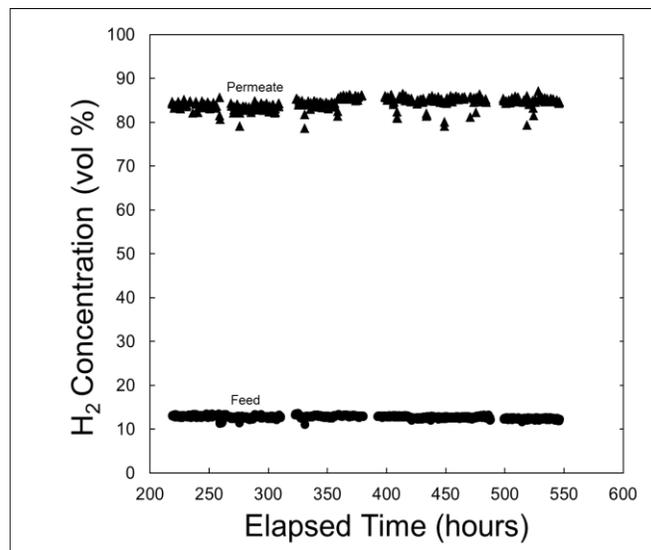


Figure 10. Hydrogen Concentration in Feed and Permeate Streams of the MTR Gen-2 Proteus Stamp Cell during R13