FLUID-BED TESTING OF GREATPOINT ENERGY'S DIRECT OXYGEN INJECTION CATALYTIC GASIFICATION PROCESS FOR SYNTHETIC NATURAL GAS AND HYDROGEN COPRODUCTION

Year 6 – Activity 1.14 – Development of a National Center for Hydrogen Technology

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ABSTRACT

The GreatPoint Energy (GPE) concept for producing synthetic natural gas and hydrogen from coal involves the catalytic gasification of coal and carbon. GPE's technology "refines" coal by employing a novel catalyst to "crack" the carbon bonds and transform the coal into clean-burning methane (natural gas) and hydrogen.

The GPE mild "catalytic" gasifier design and operating conditions result in reactor components that are less expensive and produce pipeline-grade methane and relatively high purity hydrogen. The system operates extremely efficiently on very low cost carbon sources such as lignites, subbituminous coals, tar sands, petcoke, and petroleum residual oil. In addition, GPE's catalytic coal gasification process eliminates troublesome ash removal and slagging problems, reduces maintenance requirements, and increases thermal efficiency, significantly reducing the size of the air separation plant (a system that alone accounts for 20% of the capital cost of most gasification systems) in the catalytic gasification process.

Energy & Environmental Research Center (EERC) pilot-scale gasification facilities were used to demonstrate how coal and catalyst are fed into a fluid-bed reactor with pressurized steam and a small amount of oxygen to "fluidize" the mixture and ensure constant contact between the catalyst and the carbon particles. In this environment, the catalyst facilitates multiple chemical reactions between the carbon and the steam on the surface of the coal. These reactions generate a mixture of predominantly methane, hydrogen, and carbon dioxide. Product gases from the process are sent to a gas-cleaning system where CO_2 and other contaminants are removed. In a full-scale system, catalyst would be recovered from the bottom of the gasifier and recycled back into the fluid-bed reactor. The by-products (such as sulfur, nitrogen, and CO_2) would be captured and could be sold to the chemicals and petroleum industries, resulting in near-zero hazardous air or water pollution. This technology would also be conducive to the efficient coproduction of methane and hydrogen while also generating a relatively pure CO_2 stream suitable for enhanced oil recovery (EOR) or sequestration.

Specific results of bench-scale testing in the 4- to 38-lb/hr range in the EERC pilot system demonstrated high methane yields approaching 15 mol%, with high hydrogen yields approaching 50%. This was compared to an existing catalytic gasification model developed by GPE for its process. Long-term operation was demonstrated on both Powder River Basin subbituminous coal and on petcoke feedstocks utilizing oxygen injection without creating significant bed agglomeration. Carbon conversion was greater than 80% while operating at temperatures less than 1400°F, even with the shorter-than-desired reactor height. Initial designs for the GPE gasification concept called for a height that could not be accommodated by the EERC pilot facility. More gas-phase residence time should allow the syngas to be converted even more to

methane. Another goal of producing significant quantities of highly concentrated catalyzed char for catalyst recovery and material handling studies was also successful. A Pd–Cu membrane was also successfully tested and demonstrated to produce 2.54 lb/day of hydrogen permeate, exceeding the desired hydrogen permeate production rate of 2.0 lb/day while being tested on actual coal-derived syngas that had been cleaned with advanced warm-gas cleanup systems. The membranes did not appear to suffer any performance degradation after exposure to the cleaned, warm syngas over a nominal 100-hour test.

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The GPE mild "catalytic" gasifier design and operating conditions result in reactor components that are less expensive and produce pipeline-grade methane and relatively high purity hydrogen. The system operates extremely efficiently on very low cost carbon sources such as lignites, subbituminous coals, tar sands, petcoke, and petroleum residual oil. In addition, GPE's catalytic coal gasification process eliminates troublesome ash removal and slagging problems, reduces maintenance requirements, and increases thermal efficiency, significantly reducing the size of the air separation plant (a system that alone accounts for 20% of the capital cost of most gasification systems) in the catalytic gasification process.

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APPROACH

The GreatPoint Energy (GPE) concept for producing synthetic natural gas and hydrogen from coal involves the catalytic gasification of coal and carbon. GPE is following in the footsteps of the petroleum-refining industry by implementing a more advanced and lower-cost process for refining carbon-based feedstocks. In the early days of petroleum production, oil refineries—like today's coal gasifiers—relied on intense heat called thermal cracking to break down heavy crude oil into light, usable petroleum products. In the 1940s, however, scientists discovered that a catalyst could be used to minimize the amount of heat required. This lower-cost and higher-efficiency approach quickly replaced thermal cracking in oil refineries around the world.

GPE's technology uses the same basic technique to "refine" coal by employing a novel catalyst to "crack" the carbon bonds and transform the coal into clean-burning methane (natural gas) and hydrogen.

By adding a catalyst to the coal gasification system, GPE is able to reduce the operating temperature in the gasifier and, at the same time, directly promote the reactions that yield methane (CH_4) and hydrogen (H_2). Under these mild "catalytic" conditions, less expensive reactor components are required, pipeline-grade methane is produced, and relatively high purity hydrogen can be separated while very low cost carbon sources (such as lignites, subbituminous coals, tar sands, petcoke, and petroleum resid) can be used as feedstocks.

In addition, GPE's catalytic coal gasification process reduces the potential for troublesome ash removal and slagging problems, reduces maintenance requirements, and increases thermal efficiency. Increased efficiency significantly reduces the size of the air separation plant, a system that alone can account for 20% of the capital cost of the catalytic gasification process In short, the GPE system should show a lower cost per volume of high energy syngas constituents compared to other gasifiers.

The GPE gasification process feeds coal and catalyst into the fluid-bed reactor with pressurized steam and a small amount of oxygen to "fluidize" the mixture and ensure constant contact between the catalyst and the carbon particles. In this environment, the catalyst facilitates multiple chemical reactions between the carbon and the steam on the surface of the coal. These reactions (shown below) generate a mixture of predominantly methane, hydrogen, and carbon dioxide. Product gases from the process are then sent to a gas-cleaning system where CO_2 and other contaminants are removed. In addition, the catalyst is recovered from the bottom of the gasifier and recycled back into the fluid-bed reactor.

Figure 1 illustrates the basic process to produce substitute natural gas (SNG).

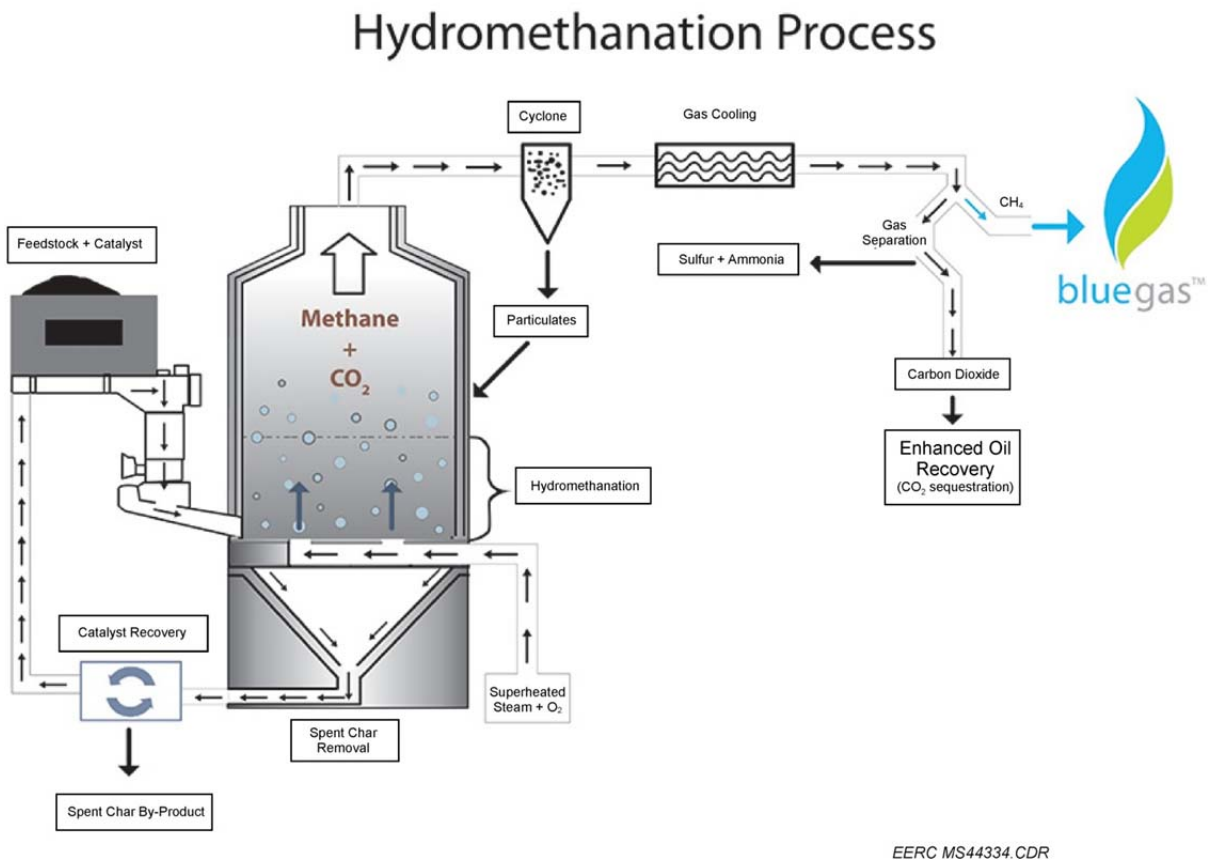

Figure 1. The basic process to produce SNG.

The overall combination of reactions (shown below) is thermally neutral, requiring no addition or removal of energy, making it highly efficient:

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow H_2 + CO$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$2C + 2H_2O \rightarrow CH_4 + CO_2$$

The proprietary sulfur-tolerant catalyst formulation is made up of abundantly available, low-cost metal materials specifically designed to promote gasification at the low temperatures where water–gas shift and methanation reactions concurrently take place. The catalyst is continuously recycled and reused within the process.

In commercial application, the by-products (such as sulfur, nitrogen, and CO_2) would be captured and sold to the chemicals and petroleum industries, resulting in near-zero hazardous air or water pollution. End products such as pure methane or hydrogen would be transported by pipeline to customers or stored. With warm-gas cleanup such as warm-gas filters, regenerable sulfur removal sorbents, and hydrogen or carbon dioxide purification, this technology could also generate a relatively pure CO_2 stream suitable for enhanced oil recovery (EOR) or sequestration.

TESTING AND RESULTS

Initial testing was performed in the Energy & Environmental Research Center (EERC) gasifier in May of 2010.

Specific run conditions such as fuel feed rates, gasifier reactor temperature, reactor pressure, fluidization rates, and syngas quality production are not reported at the request of GPE. The EERC's 600–1000-psi-rated 10–20-lb/hr fluid-bed gasifier was modified for this project and used for all testing. This system can attain nominal gasification reaction temperatures between 1500° to 2000°F and can recycle syngas while achieving full exit gas stream warm-gas cleanup. Some nitrogen dilution was used for all testing at the system pressure of 500 psig in order to achieve the desired velocities. The fine particle size of the GPE feed material (a catalyzed Powder River Basin [PRB] coal which was tested for all preliminary shakedown testing) caused feeding problems with the K-Tron feeder, so testing was done in a batch mode, using the bed material addition hopper to supply feed to the reactor. A total of 107 pounds of feedstock was processed over 10 hours of operation.

The next gasifier run took place in July of 2010. Again, a batch mode of operation was used, although the catalyzed feedstock was added to the reactor with the K-Tron feeder. A series of tests at increasing temperatures was performed over 5 days. Steam and nitrogen were used as fluidizing media.

The last three sets of conditions were longer-duration tests. The operating results for these three test periods are shown in Table 1. A total of 395 pounds of fuel was fed over 56 hours.

While the tests were successful, GPE wished to run with a longer residence time, which required building an extension on the existing gasifier riser and standpipe sections and installing additional plumbing from the gasifier outlet to the hot-gas filter vessel.

A shakedown test of the extension was performed in early November of 2010. Problems with the fuel feed system resulted in operational problems, forcing a shutdown within 30 minutes after fuel feed started.

After the feeder problem was fixed, a successful run of 8 days took place with the extension. There were still some coal feed issues, including free flow from the feeder to the reactor, significant enough to force a shutdown after 12 hours. It is possible that the relatively low bed velocity was not sufficient to maintain good fluidization, contributing to fluidization problems. A larger particle-size distribution for the feed coal and a 80% higher velocity in the bed allowed for stable operation for the remainder of the run.

Table 1. Average Gas Compositions, July 2010, mol%

	Test 1	Test 2	Test 3
Relative Temperature to Baseline	0.99	0.98	0.96
O_2/Coal wt Ratio, lb/lb	0.24	0.23	0.22
Steam/Coal wt Ratio, lb/lb	2.28	3.74	1.22
Relative Residence Time Ratio	1.018	1.04	1.00
Gas Composition			
CO	2.3	1.5	1.6
CO_2	11.4	8.7	4.4
H_2	18.6	16.8	7.8
CH_4	2.4	1.6	0.7
N_2	65.3	71.4	81.3
H_2S	0.029	0.021	0.005
Gas Composition, N_2-free			
CO	6.6	5.2	11.0
CO_2	32.9	30.4	30.3
H_2	53.6	58.7	53.8
CH_4	6.9	5.6	4.8
H_2S	0.084	0.073	0.034

For the first week, a catalyzed PRB coal was used as the feedstock; the last 2 days, a catalyzed petroleum coke was used. The average gas compositions are found in Table 2. Tests 1 through 8 used the PRB coal feedstock; Tests 9–11 represent petroleum coke feed. Test 8 was a "hot spot" test to understand exotherm formation in the reactor, at very high coal feed and oxygen flow rates. The unit was shut down at the end of this test.

A total of 393 pounds of coal was fed over 58 hours; 360 pounds of petroleum coke was fed over 50 hours.

The next run, performed in August 2011, had three primary goals:

1. Generate sufficient concentrated catalytic char/bed material to conduct larger catalyst recovery studies at GPE.

2. Operate the gasifier for long test periods of greater than 12 hours at each condition to get good material balance information while also testing the effect of recycling some syngas to the gasifier in order to understand the catalytic bed chemistry occurring in the upper part of the bed

3. Test a hydrogen separation membrane for its ability to separate hydrogen from the methane-rich gas stream.

Table 2. Average Gas Compositions, November 2010, mol%

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Rel. Temp to Baseline	0.92	0.91	0.97	0.98	0.94	0.99
O_2/Coal wt Ratio, lb/lb	0.17	0.14	0.25	0.26	0.12	0.26
Steam/Coal wt Ratio, lb/lb	0.87	0.84	0.89	0.86	1.36	0.95
Rel. Residence Time Ratio	4.56	3.89	2.92	3.28	3.07	2.63
Gas Composition						
CO	1.16	1.28	1.91	3.24	2.18	2.56
CO_2	3.88	3.33	3.04	4.57	5.16	3.85
H_2	6.30	6.11	5.79	8.37	10.73	7.32
CH_4	1.03	0.89	0.75	1.28	1.22	0.82
N_2	86.15	87.12	87.23	81.72	81.51	84.09
H_2S	0.0	0.00	0.00	0.00	0.01	0.00
Gas Composition, N_2-free						
CO	9.38	11.02	16.62	18.56	11.30	17.59
CO_2	31.37	28.68	26.46	26.17	26.74	26.46
H_2	50.93	52.63	50.39	47.94	55.60	50.31
CH_4	8.33	7.67	6.53	7.33	6.32	5.64
H_2S	0.00	0.00	0.00	0.00	0.00	0.00
	Test 7	Test 8	Test 9	Test 10	Test 11	
Rel. Temp to Baseline	0.99	0.94	0.99	0.99	0.99	
O_2/Coal wt Ratio, lb/lb	0.26	0.24	0.28	0.19	0.18	
Steam/Coal wt Ratio, lb/lb	2.18	0.93	1.83	4.07	3.81	
Rel. Residence Time Ratio	2.67	2.65	1.99	2.10	2.02	
Gas Composition						
CO	1.89	5.56	2.12	2.29	2.29	
CO_2	4.82	26.23	2.92	5.46	5.61	
H_2	9.24	26.95	6.28	10.59	10.59	
CH_4	0.72	8.74	0.55	0.86	0.85	
N_2	82.41	31.58	87.06	79.49	79.34	
H_2S	0.01	0.09	0.16	0.22	0.25	
Gas Composition, N_2-free						
CO	11.33	8.23	17.62	11.79	11.69	
CO_2	28.90	38.82	24.27	28.12	28.64	
H_2	55.40	39.88	52.20	54.53	54.06	
CH_4	4.32	12.93	4.57	4.43	4.34	
H_2S	0.06	0.13	1.33	1.13	1.28	

Prerun calibrations were started and completed on August 18–19, 2011; however, some operating problems were experienced with the K-Tron feeder. The gasification testing was started on August 22; however, the operating problems continued to get worse until the feeder quit working altogether on the evening of August 23. At this point, and in consultation with GPE personnel already on-site, it was decided to concentrate the catalyst on the char in a batch mode, utilizing the bed material addition vessel to charge the reactor with low-catalyst-concentration char and then react the bed with steam and oxygen for approximately 4 hours to consume over

half of the carbon in the bed and concentrate the catalyst to the desired range for GPE's catalyst recovery testing. The coal feeder was isolated and dissembled to determine what had failed on the feeder. After examination, it was determined that both the motor brushes and the load cell had failed because of corrosion of some electrical wires and components. New parts were ordered, but it was determined that it would be a week before the parts could arrive and the feed system could be repaired. At this point, it was decided that the membrane testing would be postponed until the feeder could be fixed, but GPE felt that continuing to generate concentrated bed material in a batch mode would still achieve the first test objective. Over the next 10 days, the EERC continued to generate about four batches a day of concentrated bed material. This batch testing generated 234 lb of bed material and 53 lb of filter char for GPE catalyst recovery and solids flowability testing.

The feeder was repaired toward the end of the batch testing, but the decision was made to continue this batch processing because the process for generating the desired concentration was well established, and it was felt that continuous processing would take too long to start generating the desired catalyst concentration by the end of the testing period. A decision was made to conduct another week of testing September 26–30, 2011. This test was conducted in a continuous manner after the K-Tron coal feeder was fixed and utilized syngas recycle. GPE was interested in utilizing syngas recycle to better understand the catalytic gas-phase chemistry that occurs in the upper regions of the bed after the oxygen and steam react to form hydrogen and carbon monoxide. The water–gas shift (WGS) reaction and the carbon hydrogenation reactions are catalyzed and predominantly occur in the higher regions of the bed. The utilization of syngas recycle also decreases the nitrogen concentration in the exit gas which improves the membrane performance. A sour shift catalyst bed and a regenerable sulfur sorbent were also utilized downstream of the gasifier to increase the hydrogen yield for the membrane testing.

Average gas compositions reflecting the utilization of the shift catalyst and sulfur sorbent for the continuous testing are shown in Table 3. The nature of the GPE gasification process for increasing methane and hydrogen is evident in the average gas compositions.

HYDROGEN SEPARATION MEMBRANE TESTING

Introduction

The objective of this portion of the testing was to validate hydrogen permeate, flux, and recovery of a single membrane assembly while adding cumulative operational hours on coal-derived syngas. The EERC and the U.S. Department of Energy's (DOE's) National Energy Technology Laboratory (NETL) partnered to evaluate the hydrogen production performance of a hydrogen separation membrane. This test was conducted in conjunction with GPE's testing of its catalyzed coal for the production of hydrogen-separation-membrane-compatible syngas. The EERC had previously evaluated the performance of several hydrogen separation membranes on coal-derived syngas. This hydrogen membrane test builds on prior hydrogen separation membrane testing work.

Table 3. Average Gas Compositions, September 2011, mol%

	Test 1	Test 2	Test 3
Rel. Temp to Baseline	1.06	1.06	1.06
O_2/Coal wt Ratio, lb/lb	0.45	0.43	0.34
Steam/Coal wt Ratio, lb/lb	5.23	4.97	3.75
Relative Residence Time Ratio	2.59	2.70	2.62
Gas Composition			
CO	0.3	0.2	0.3
CO_2	25.5	26.3	25.0
H_2	30.8	31.8	28.6
CH_4	7.8	9.0	6.4
N_2	35.9	32.7	40.4
H_2S	0.01	0.00	0.00
Gas Composition, N_2-free			
CO	0.5	0.3	0.5
CO_2	39.8	39.1	41.9
H_2	48.0	47.3	48.0
CH_4	12.2	13.4	10.7
H_2S	0.02	0.00	0.00

Background

Efficient and cost-effective membranes for the separation of hydrogen and CO_2 represent a potential cost-effective method for simultaneously producing power, hydrogen, and/or chemicals while CO_2 can be sequestered. Significant progress has been made over the past decade in producing membranes that can effectively separate hydrogen from the syngas stream, leaving a relatively pure stream of CO_2 available at high pressure for sequestration. Cost-effective CO_2 separation is a significant technical hurdle, with a potential 84% increase in cost of electricity produced for existing pulverized coal power plants with retrofit carbon capture (1). Therefore, novel approaches to the problem are required, including hydrogen and CO_2 separation membranes.

Five main types of membranes are currently under development: dense polymer, microporous ceramic, porous carbon, dense metallic, and dense ceramic (2). Of these types, dense metallic and dense ceramic have the highest hydrogen selectivity. Dense metallic membranes also have very high hydrogen flux rates, making them potential candidates for large-scale commercial application if poisoning issues can be overcome. Palladium is the typical base metal for metallic membranes, and alloy combinations such as Pd–Cu, Pd–Au, and Pd–Ag have been tested. Many other formulations exist, but most are closely guarded trade secrets.

Hydrogen separation membrane development to date has occurred mainly on simulated mixtures of syngas. Impurities from coal-derived syngas that could poison a hydrogen separation membrane include H_2S, COS, NH_3, CO, and HCl. Long-term success of hydrogen separation membranes will require long-term exposure to coal-derived syngas to understand the impact of

the impurities. While the majority of the impurities will be removed in a gas cleanup process, concentrations to less than 1 ppm may be required for long-term viability.

The development of warm-gas cleanup techniques is essential to the successful deployment of hydrogen separation membranes. Metallic membranes operate optimally between 300° and 600°C (572° and 1112°F). Cold-gas-cleaning techniques that cool the syngas to ambient temperature or less will result in a substantial energy penalty from having to reheat the syngas before hydrogen separation. Additionally, WGS catalysts require higher temperatures to operate efficiently, and some level of heating is achieved in the shift catalyst bed.

Description of Test

Syngas was generated by the EERC's fluid-bed gasifier (FBG) using GPE's catalyzed PRB coal. Particulate was removed with a hot-gas filter vessel. The filter is able to achieve near absolute capture. WGS was achieved through the use of Katalco K8-11 sour gas shift catalyst to maximize hydrogen and minimize CO concentrations in the syngas. The warm-gas-conditioning train is capable of operating with up to six fixed beds of catalysts and sorbents, although only four fixed beds were utilized for this test. Figure 2 shows the warm-gas-conditioning train. Syngas flows from the filter, on the right, to the membrane system, on the left. For this test, Fixed Bed 1 and Fixed Bed 2 were used for WGS, with the first fixed bed operating at approximately 300°C (575°F) and the second at approximately 275°C (525°F). RVS-1 solid sorbent from Sud-Chemie was used in Fixed Bed 3 and Fixed Bed 4 to remove sulfur. Fixed Beds 3 and 4 are used in an alternating manner. Once one becomes saturated and sulfur breakthrough is observed, the other fixed bed is brought online while the first is isolated for regeneration. Only Fixed Bed 3 was used during this test since no significant sulfur breakthrough was detected.

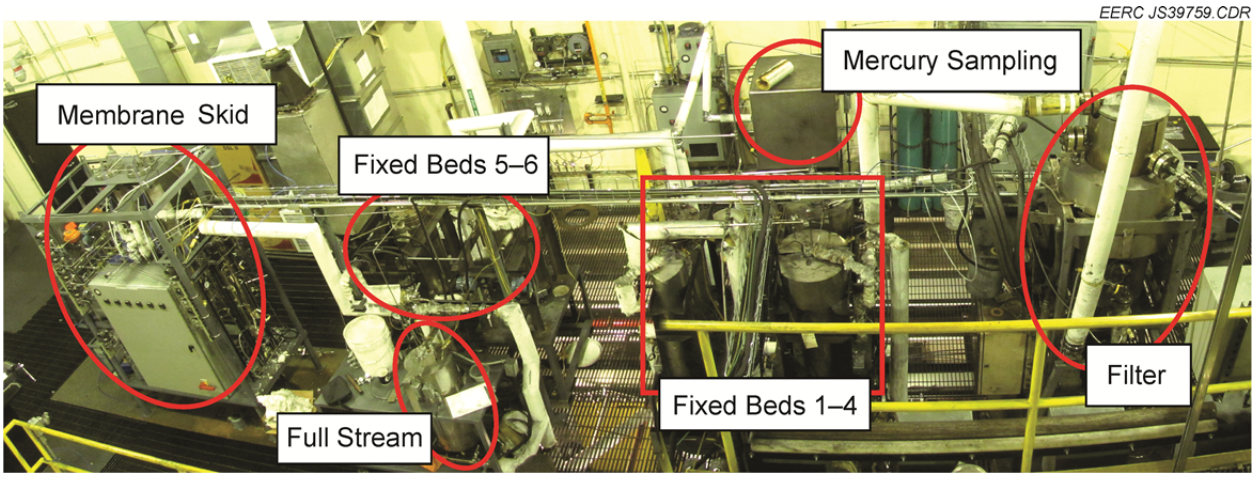

Figure 2. Warm-gas-conditioning train.

The EERC's hydrogen membrane test system (HMTS) was used to perform testing of the membrane supplied by the membrane developer. The HMTS is capable of simultaneously testing multiple membranes. During this 1-week test, only one membrane was installed and tested. The membrane tested was a metallic Pd–Cu-based membrane that is capable of achieving high flux rates and shows resistance to sulfur poisoning. The membrane was sized to take approximately 200 scfh of syngas from the gasifier, with the intent to be able to separate 2 lb/day or more of hydrogen. The membrane operates at 932°F and can take pressures up to 500 psi. The membrane was not designed to use a permeate sweep gas.

Figure 3 shows the membrane assembly, as it was installed in the heater. The HMTS is composed of multiple controlled heaters; purge gas mass flow controllers; water-cooled quench pots for postseparation gas cooling; raffinate flow control; and instrumentation for temperature, pressure, flow measurement, and gas analysis. The HMTS uses a high-speed data acquisition and control system. User control and data logging are via a remotely located personal computer. The control computer utilizes a custom-written program with a graphical user interface. The control program was modified to meet the specific needs of the test.

Figure 3. Hydrogen membrane test system.

Figure 4 shows the sampling locations for the system. The Varian gas chromatograph (GC) and the laser gas analyzer (LGA) 035 were connected to Sample Port (SP) C while the membrane was in operation. SP-C was used for taking Dräger tube samples downstream of the bulk desulfurization outlet to monitor for sulfur breakthrough. Both cold- and hot-gas samples may be drawn for Dräger tube sampling through SP-C. The Varian GC utilizes a pulsed flame photometric detector and is capable of detecting sulfur levels under 1 ppm. The Yokogawa GC and LGA-039 were connected to SP-D. This point was monitored as part of the gasifier's control and operation. LGA-049 was used to sample the permeate and raffinate from the membrane at SP-E and SP-F, respectively. SP-A and SP-B are typically used to evaluate WGS catalyst performance. These two ports were not used during this test.

Trace metal sampling was performed at the SP-C_{HOT} sampling location, before the hydrogen separation membranes. Sampling at this location measures the trace concentrations that the hydrogen separation membranes are exposed to. Mercury concentrations were determined by syngas sampling using sorbent traps (Method 30B). Previous research at the EERC indicated that sorbent traps were able to provide reliable and accurate syngas mercury concentrations. The samples were collected using Ohio Lumex sorbent traps and analyzed using an Ohio Lumex RA915+ mercury analyzer. This instrument utilizes a pyrolysis technique followed by Zeeman atomic absorption detection. Additional trace elements were measured at Port C using the Mercury Speciation Adsorption (MESA) method.

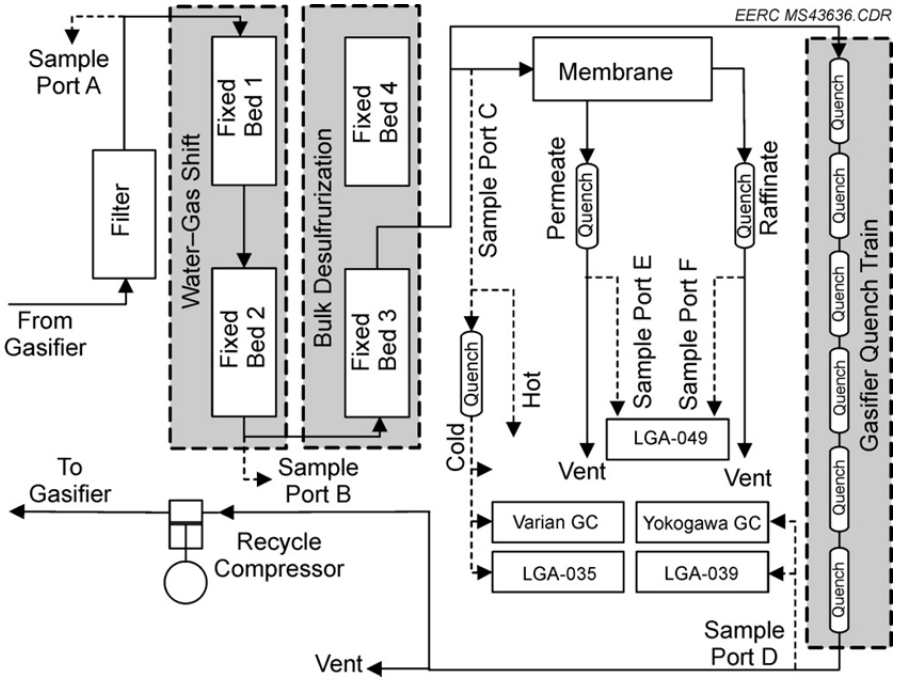

Figure 4. Sampling locations.

Table 4 shows the sampling plan for warm-gas cleanup and hydrogen separation membranes. Dräger tube measurement of H_2S at SP-C_{COLD} was planned once each 8-hour shift. As breakthrough became evident, the H_2S measurements were done more frequently to ensure that a 10-ppm concentration was not exceeded. If the H_2S level would trend toward this limit, Fixed Bed 4 would be brought online while Fixed Bed 3 was regenerated offline.

Hydrogen Membrane Results and Discussion

The objective of this test was to validate hydrogen permeate, flux, and recovery of a single membrane assembly while cumulative operational hours were added. EERC's pilot-scale pressurized FBG was used to produce syngas. WGS catalyst was used to enhance the syngas hydrogen concentration, and solid sorbents were used for warm-gas cleanup. The separation membrane was exposed to coal-derived syngas for approximately 97 hours. The process conditions of the FBG were highly variable during the first two-thirds of the testing. For this reason, performance data from the final 33 hours of testing the hydrogen membrane were analyzed. H_2S was maintained below a 2-ppmv level.

The membrane achieved average hydrogen flux of 13.6 $ft^3ft^{-2}h^{-1}$, with a recovery of 54.5% of total hydrogen, and permeate of 2.54 lb day^{-1}. Figure 5 gives results for a composite set of membrane performance graphs that includes H_2 flux, H_2 permeate, total flows, and system temperature. Syngas was supplied to the HMTS at 2100 on September 26, 2011. Raffinate and permeate flows were measured, with temperature and pressure correction being made in real time. Flow through the separator was controlled manually by a back-pressure control valve. The goal was to use as much of the gasifier's product gas as possible without causing the gasifier pressure to drop. Because of fluctuations in the operation of the gasifier, flow through the HMTS was varied to maintain gasifier pressure. The total syngas flow across the membrane was 9200 scf.

Table 4. Coal Syngas Sampling and Analysis Plan

Sample Port/ Location	Analyzers for Bulk Gas Composition	Dräger Tubes				Trace Metal
		H_2S	NH_3	HCN	HCl	
Sample Port A	None	None	None	None	None	None
Sample Port B	None	None	None	None	None	None
Sample Port C	Continuous Varian GC and LGA-035	1x/shift (cold)	1x/shift (hot)	1x/shift (hot)	1x/shift (hot)	1x/week (hot)
Sample Port D	Continuous Yokogawa GC and LGA-039	None	None	None	None	None
Sample Port E	Intermittent LGA-049	None	None	None	None	None
Sample Port F	Intermittent LGA-049	None	N/A	N/A	N/A	N/A

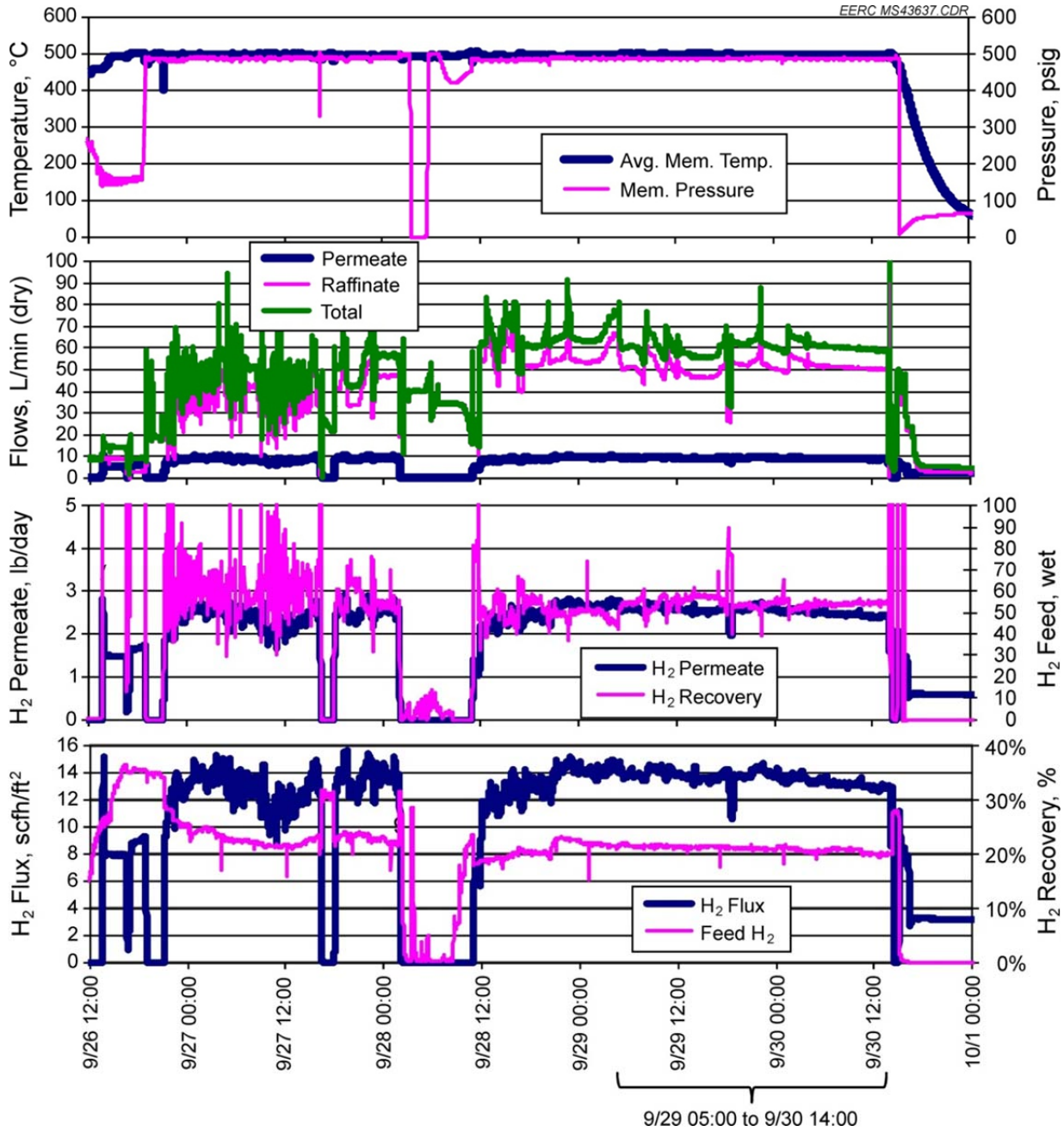

Figure 5. Membrane performance graphs.

A trace metal carbon trap was used midway through the test period to examine chromium, nickel, selenium, and arsenic concentrations in the syngas. The measured concentration results were As = 1.174 µg/m^3, Cr = 8.198 µg/m^3, and Ni = 74.79 µg/m^3, with all other species being nondetects. Dräger tube samples were drawn 25 times during the test period. The averages are as follows: H_2S = 0.67 ppm, HCl = 0.015% vol, HCN = 0 ppm, and NH_4 = 0.2 ppm. The membrane appeared to operate successfully over the duration of the testing, with no obvious decrease in performance.

CONCLUSIONS

Catalytic gasification testing of the GPE catalytic gasification process was successfully completed. This testing demonstrated high methane yields approaching 15 mol%, with high hydrogen yields approaching 50%. Long-term operation was demonstrated on both PRB subbituminous coal and on petcoke feedstocks utilizing oxygen injection without creating significant bed agglomeration. Carbon conversion was greater than 80% when operating temperatures were less than 1400°F, even with the shorter-than-desired reactor height.

The system also proved successful in producing significant quantities of highly concentrated catalyzed char for catalyst recovery and material handling studies.

With respect to hydrogen membrane separation, a Pd–Cu membrane was also successfully tested and demonstrated to exceed the desired hydrogen permeate production rate of 2.0 lb/day while being tested on actual coal-derived syngas that had been cleaned with advanced warm-gas cleanup systems. The membranes did not appear to suffer any performance degradation after exposure to the cleaned warm syngas over a near 100-hour test.

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