Technology Developer Run Report

DOE Cooperative Agreement No. DE-FE0012965

DOE Project Title: Development of a Precombustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes

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DISCLAIMER

1. PROJECT OBJECTIVES/GOAL

SRI International (SRI) tested a membrane skid installed with high-temperature stable polybenzimidazole hollow-fiber membrane (PBI HFM) modules for separating H_2 and CO_2 from syngas during the G5 gasifier run at the National Carbon Capture Center (NCCC) gasifier site, Wilsonville, AL.

The primary objectives of the project are to evaluate, at a bench-scale size, a technically and economically viable CO_2 capture system based on a high-temperature PBI hollow fiber polymer membrane separation system, and to optimize the process for integration of that system into an integrated gasification combined cycle (IGCC) plant. The specific objectives of the proposed project are to: (1) collect laboratory data for separating hydrogen from simulated synthesis gas using PBI-based membrane modules; (2) fabricate membrane modules to process a syngas stream (50 kW_{th}) equivalent to that of shifted gas from an oxygen-blown gasifier; (3) obtain design and steady-state performance data for membrane modules using syngas from an operating coal gasifier; (4) and conduct the process techno-economic analysis (TEA) and environmental health and safety (EH&S) assessment.

The overall goal is to develop PBI membrane-based H_2/CO_2 separation technology for IGCC power plants that shows significant progress towards meeting the overall DOE Carbon Capture Program performance goal of 90% CO_2 capture rate at a cost of $40/tonne of CO_2 captured by 2025. To show progress toward meeting the 2025 DOE program goal, the near-term goal for this project is to reach PBI membrane-based performance targets of 100-125 GPU for gas permeance and 20-25 selectivity for H_2 over CO_2.

2. OBJECTIVES ACHEIVED DURING THE RUN AND ACCOMPLISHMENTS

- Successful commissioning and operation of the PBI skid at the field site. The process control equipment and the individual components of the skid performed well during this testing period. Two pairs of 4-in modules, each pair of a different design, were tested under a variety of feed gas conditions including doping the syngas with supplemental hydrogen and carbon dioxide to more closely match the composition of an oxygen blown-gasifier, which is the design goal feed gas to achieve optimally high hydrogen recovery and carbon dioxide capture.
- The skid was operated the under various operating conditions (dynamic and steady state). The parameters varied include gas composition, gas feed rate, pressure differential, temperature, and stage cut. The data were collected for air-blown and oxygen-blown

gasifier syngas compositions for future long-term scale-up testing and for validating the techno-economic analysis.

- The skid was operated for 600 hours and received Syngas or Syngas with supplemental H_2 and CO_2 for about 500 hours. During this testing, it was
  - Demonstrated that a greater than 90% CO_2 capture is possible with air-blown syngas at temperatures >180˚ C and with a stage-cut less than 40%;
  - Observed a hydrogen recovery greater (~99%) at the higher stage cut (60%) with simulated oxygen-blown syngas;
  - Observed similar or better performance in large modules (4-in modules at NCCC) compared to smaller modules (1-in modules at SRI);
  - Demonstrated that the H_2/CO_2 selectivity of PFI HFMs increased with increasing temperature (this behavior is a unique property of PBI HFMS and the conventional polymer membranes show the opposite effect).

3. IMPACT OF THE PROJECT/PROJECT BENEFITS/PROJECT DESCRIPTION

Successful development of this technology will greatly reduce the anthropogenic emission of CO_2 into the atmosphere. Despite the slowing electricity demand growth, low natural gas prices, and plant retirements, coal-fired power plants are expected to contribute to about 38% of total U.S. CO_2 emissions in 2035, according to the Annual Energy Outlook 2012 with Projections to 2035, Report # DE/EIA-0383(2012), June 2012. SRI is investigating a technology that can recover CO_2 from pre-combustion syngas streams at a cost less than $40/tonne and high purity that makes installing CO_2 recovery equipment more affordable for utilities and may result in opportunities to use the CO_2 in commercial applications, such as enhanced oil recovery or chemical production operations.

Brief Description of Technology

The current project entails the high-temperature separation of the CO_2 from a syngas stream from an IGCC plant containing CO_2, H_2, CO, steam, and other trace-level gases. The separation process uses high-temperature, hydrogen-selective, stable, PBI-polymer-based asymmetric hollow-fiber membranes. Figure 1 depicts the integration of a membrane-based system in an IGCC plant. The system will be situated downstream of the sour gas shift reactors. The gas stream will be cooled to above its dew point, and the membrane module will be used to separate H_2 and steam from the rest of the syngas stream. The permeate H_2, acid gasses (a few percent) and steam, along with the sweep gas N_2, will be sent to the turbine unit; CO_2 and other trace permeate gases will be sent to a high-pressure processing unit to convert H_2S to S by the Claus process, and remaining gases will be compressed to pipeline pressure.

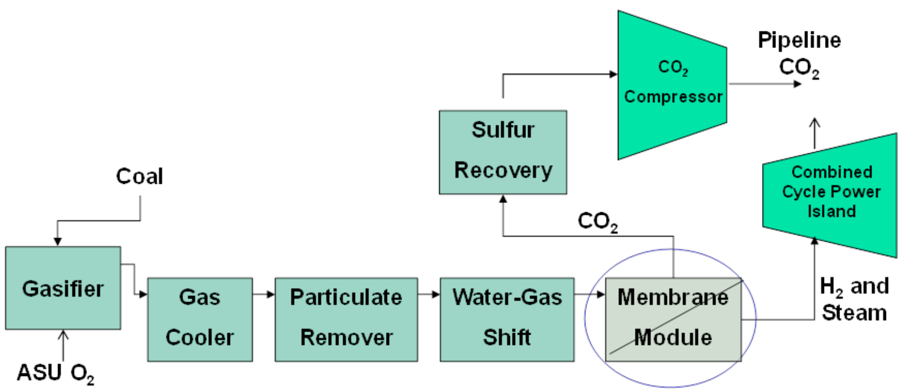

Figure 1. Block flow diagram.

Advantages of the Technology

A significant advantage of membrane technology is the ability to provide a concentrated CO_2 stream at a pressure similar to the syngas feed pressure—typically ~ 300-800 psig depending on gasifier type, process location, and other process variables—and at much higher than that possible with a physical solvent (~ 25 psig). This availability of CO_2 at high pressures typically results in at least a 5% decrease in the cost of electricity (COE) for the capture and compression of CO_2 (SRI final report, DE-FC26-07NE43090). In this technology, a syngas stream containing CO_2, H_2, steam, and H_2S among other gases such as CO and CH_4 is fed to one side of the fiber bundle at high pressures. H_2 and steam permeate through the membrane, leaving CO_2 and H_2S at nearly the syngas pressure.

Note: One of the major advantages of PBI HFM is that it has increased H_2/CO_2 selectivity with increase in temperature as compared to other polymeric membranes.

4. WHAT WAS DONE

The field testing was successfully completed during March - April 2017 and successfully demonstrated the operability of the PBI HFM modules under air-blown and oxygen-blown (by H_2 and CO_2 doping) gasifier conditions which was the main objective of this test campaign. Two pairs of 4-in modules, each pair of a different design, were tested under a variety of feed gas conditions including doping the syngas with supplemental hydrogen and carbon dioxide to more closely approximate the composition of an oxygen blown-gasifier which is the design goal feed gas to achieve optimally high hydrogen recovery and carbon dioxide capture. The modules were piped in parallel so they could be operated to together to process a 50 kW_{th} feed or tested individually.

During the test campaign, the module identified as TS-1(surface area: 6 m^2) that had SRI GEN-1 fibers was continuously operated for 500 hours with feeds of either syngas, or syngas with added H_2 and CO_2 at varying temperature and pressure conditions to evaluate its performance as a function of stage cut and different H_2 and CO_2 concentrations. In parallel, SRI also tested GEN-2 fibers in a module identified as TS-2 (surface area: 6 m^2) for 48 hours to measure its selectivity with the syngas gas feed doped with added H_2 and CO_2.

Section below provides some of the field testing details.

Membrane Skid Pre-testing

Before shipping the skid to the NCCC, a series of preliminary tests were conducted at SRI. The skid testing at SRI included (1) evaluation of the stability of the epoxy in large-scale modules, (2) leak testing through the epoxy, and (3) testing of modules fabricated by the industrial partner using SRI PBI HFMs. For the epoxy stability evaluation, SRI fabricated several 2-in and 4-in modules at SRI. These modules were heat treated under varying conditions and installed in the skid. Each module was tested for over 10 hours and removed from the skid to evaluate the nature of the epoxy potting. During the short-term testing performed at SRI with CO_2 and N_2 up to 150˚C, no epoxy delamination was found.

Membrane Skid Testing at the NCCC

The PBI HFM field testing at the NCCC was successfully conducted in March - April 2017. The demonstration of the gas separation performance of the PBI HFM modules and the operability of the skid under air-blown gasifier conditions was the main objective of this test campaign. We tested two types of 4-in (two different potting configurations) modules under a variety of conditions including supplemental hydrogen and carbon dioxide doping to the syngas. The PBI HFM performance exceeded the expectations and the goals of the project. Table 1 below shows the timeline of HFM skid testing activities performed. Figures 2 and 3 are photographs taken during the skid transportation and just after installation at the NCCC.

Table 1. Activities and timeline related to PBI skid testing at the NCCC.

Task	Date
Shipping of the skid from SRI to the NCCC	Feb 23- March 1
Placement and installation at the NCCC	Week of March 13
Installation of gas/electrical connections at the NCCC	Week of March 20

Shakedown testing at the NCCC	Week of March 27
Skid testing with syngas – number of different fiber modules	April 2 to 14
Skid testing with syngas – parametric testing	April 7 to 17
Skid testing with syngas doped with H_2 and CO_2	April 10 to 28
Skid testing with syngas – long-term testing with continuous operation	April 6 to 28

Figure 2. Photograph of the skid being loaded to a truck for transportation to the NCCC.

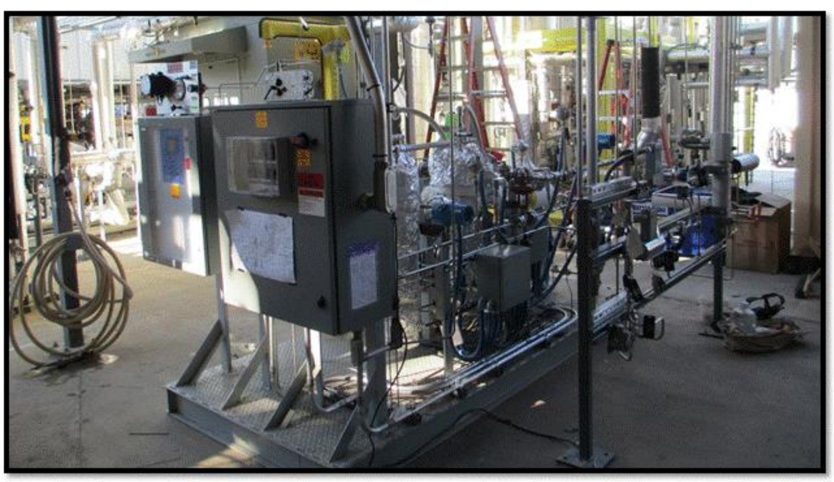

Figure 3. Photograph of the skid installed at the NCCC.

The SRI team arrived at the NCCC the week of March 13 to install the skid. The week of March 20, the NCCC staff completed the utility connections to the SRI skid. When the syngas became available, the SRI technical team arrived at the NCCC on April 2nd to test the system. The SRI skid is designed with the capability of testing multiple membrane elements. During the week of April 2nd, the team tested the performance of four membrane modules.

The PBI skid has the capability to run modules in parallel, making it easier to exchange modules when needed. During the entire current run campaign, a module identified as TS-1(6 m^2) that has SRI GEN1 fibers was continuously exposed to either the syngas, N_2, or syngas doped with H_2 and CO_2 at varying temperatures, pressure conditions to evaluate performance as a function of stage cut, and different H_2 and CO_2 concentrations. In parallel, we also tested SRI GEN-2 fibers in a module identified as TS-2 (6 m^2) to measure its selectivity with doped H_2 and CO_2.

Test Matrix

One of the key goals of the test campaign at the NCCC is to collect the data to evaluate the best operating conditions for PBI HFM to achieve 90% CO_2 capture with high H_2 recovery. For this purpose, a performance data base was generated at SRI using 1-in modules. Based on the lessons learned from that study, SRI formulated a simple parametric testing matrix for the NCCC testing and it is given in Table 2. The parameters varied include gas composition, gas feed rate, pressure differential, temperature, and stage cut.

Table 2. Sample parametric matrix for generating data for the performance database.

Test Parameter	Range	Unit
Temperature	80 to 215	°C
Pressure	50 to 170	psig
Gas composition	Variable	slpm
Stage cut	0.2-0.7	
H_2/CO_2 selectivity	10 to 30	
H_2 in syngas	12 to 60	%
CO_2 in syngas	5 to 40	%

5. TEST RESULTS

The results in the Figures below show the effects of changes in temperature, pressure and stage-cut on the membrane performance. The TS-1 module tested had SRI GEN1 fibers (GPU ~ 150, H_2/CO_2 selectivity ~ 25 at 200˚C and 200 psi) and the TS-2 module had SRI GEN-2 fibers (GPU ~ 100, H_2/CO_2 selectivity ~ 40 at 200˚C, 150 psi). The TS-1 module was operated continuously for about 500 hours, and the TS-2 module was operated continuously for about 48 hours.

Temperature Effect

Figure 4 shows the overall performance of the TS-1 module with respect to CO_2 capture as function of temperature when the feed is un-doped syngas. As predicted by the database, the CO_2

capture increased with increasing temperature. Greater than 90% CO_2 capture is possible with air-blown syngas at temperatures >180˚ C and with a stage-cut less than 40%.

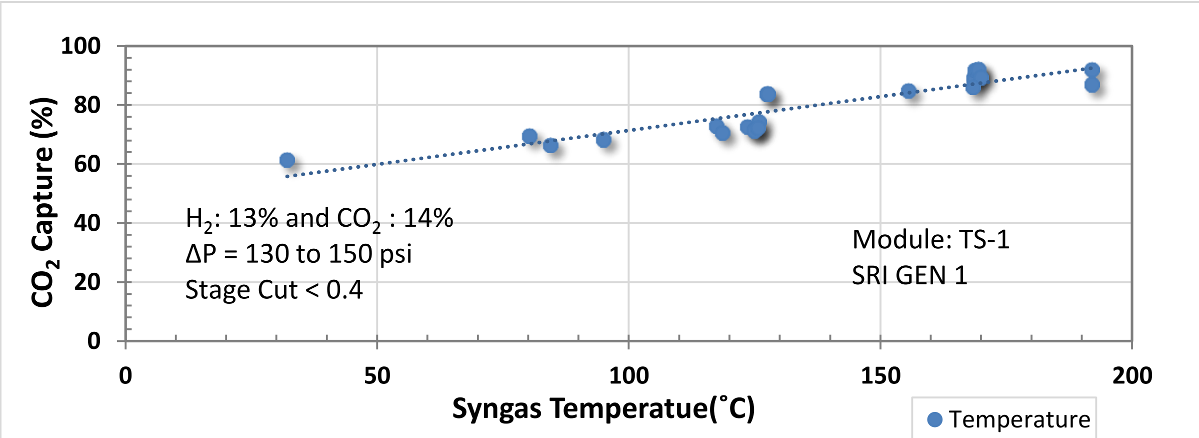

Figure 4. Observed CO_2 capture for the TS-1 membrane element with changing temperature when operating with syngas.

Figure 5 shows that the H_2/CO_2 selectivity in the TS-2 module increased with increasing temperature. This behavior is a unique property of PBI HFMS (Note: conventional polymer membranes show the opposite effect). Figure 5 also shows the comparison of the perm-selectivity data for the TS-1with GEN-1 fibers and the data from the 1-in module testing at SRI with GEN-1 fibers. The 1-in GEN-1 data shows that the TS-1 module with GEN-1 fibers would require operating it above 190˚C to achieve H_2/CO_2 selectivity of 25. In comparison the TS-2 module with GEN-2 fibers achieves the same selectivity at temperatures less than 140˚C. The NCCC field test conditions confirmed that the GEN-2 fibers are superior to the GEN-1 fibers.

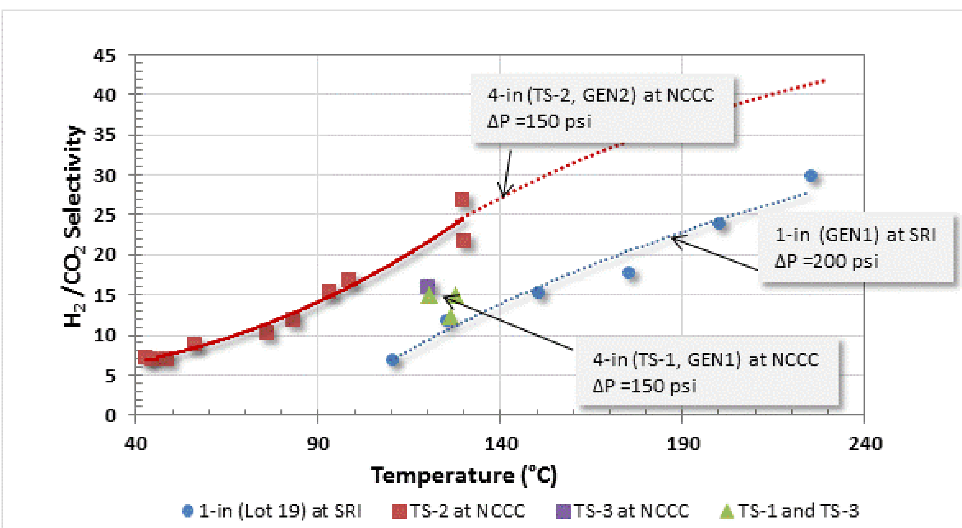

Figure 5. Comparison of measured H_2/CO_2 selectivity for GEN-1 and GEN-2 modules.

Additional data for GEN-2 measured at NCCC are given in Figures 6 and 7. Figure 6 shows H_2 and CO_2 permeances in the TS-2 module under varying temperatures at a constant pressure differential, and Figure 7 shows the data for TS-2 module under varying pressure differentials at a constant temperature.

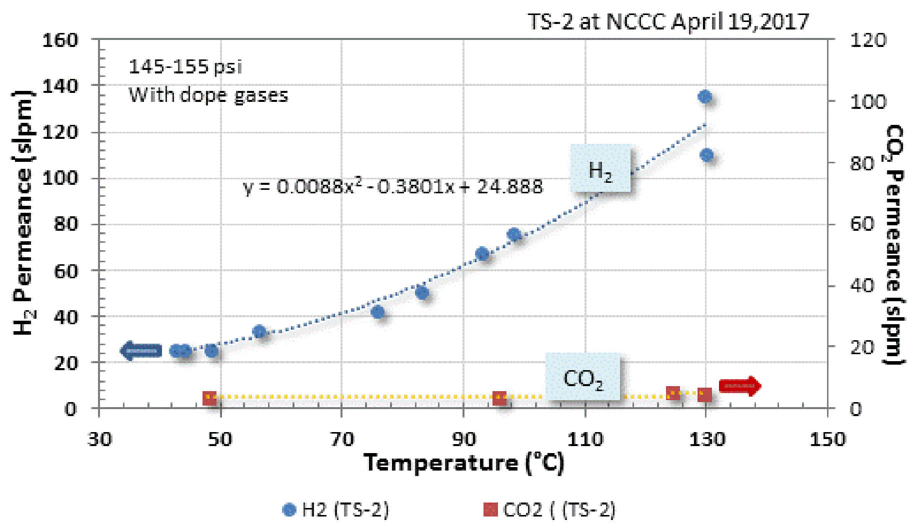

Figure 6. Measured H_2 and CO_2 permeances at the NCCC for the TS-2 (GEN-2) module at varying temperatures under a pressure differential of 145 to 155 psi.

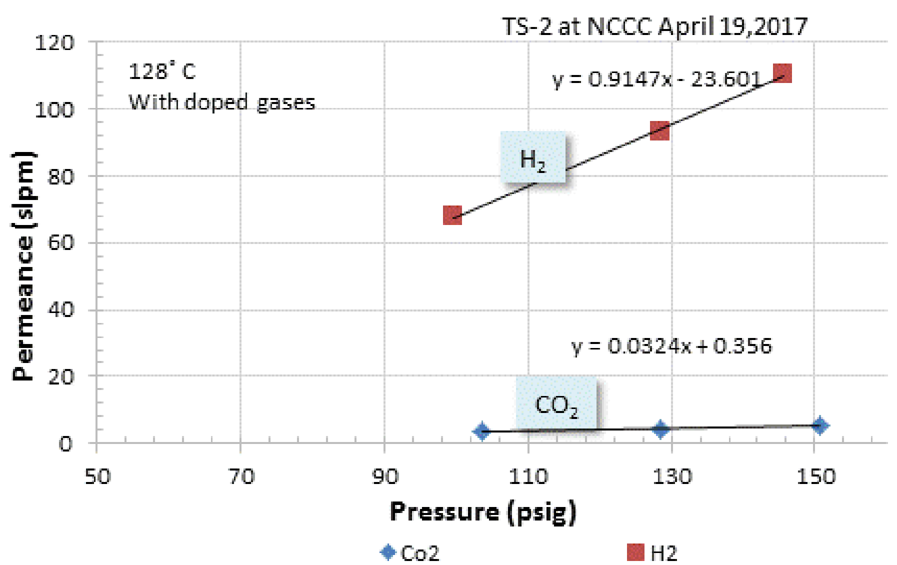

Figure 7. Measured H_2 and CO_2 permeances at the NCCC for the TS-2 (GEN-2) module with varying pressures at 128˚C

Membrane Testing with Syngas only and Syngas Doped with additional H_2 and CO_2

From April 10 through April 28, the TS-1 module was tested with varying stage-cuts and supplied with either a syngas only feed or a syngas feed doped with additional (~ 50%) H_2 and

CO_2. The overall observed performance data is given in Figure 8. As expected, the hydrogen recovery is greater (~99%) at the higher stage cut (0.6), while the CO_2 recovery, as shown in Figure 4, is higher (> 90%) at the lower stage cut (0.4). Our data also shows that, at temperatures above 150˚C, the hydrogen recovery depends mostly on the operating stage cut. The modules tested were constructed with a dead-end design, i.e., fiber shell-side gas feed with one end of fiber bore-side sealed in the potted module. We expect much improved performance for the membranes potted with both bore-side ends open to allow a bore-side flow-through configuration enabling the use of N_2 permeate sweep gas to further optimize higher hydrogen recovery and carbon dioxide capture.

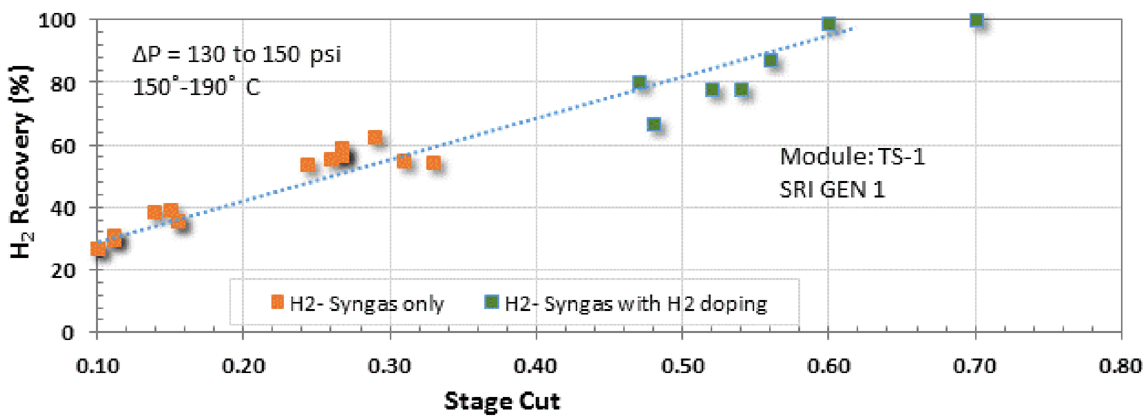

Figure 8. Observed hydrogen recovery with varying stage cuts in the temperature range 150 – 190˚C and a pressure differential of 130 to 150 psi for the syngas-only condition and for syngas with doped with H_2.

During the test campaign, a preliminary investigation of the effect of CO_2 concentration on the CO_2 capture from syngas was conducted. The lowest CO_2 concentration point (7%) was collected when the gasifier was operating under an offset condition and the higher CO_2 concentration data points were collected by doping the syngas with added CO_2. The results show that it is possible to achieve a 90% CO_2 capture when the syngas stream contains a higher CO_2 fraction, e.g., greater than 30%, which is a typical CO_2 concentration in the design goal of oxygen-blown gasifier syngas feed. Also, the oxygen blown gasifier syngas typically contains about 23% water (steam). The PBI HFM is highly selective for water. Water partial pressure in the permeate stream would increase the PBI HFM H_2 permeation driving force across the membrane by lowering H_2 partial pressure in the permeate, which further optimizes higher H_2 recovery and CO_2 capture.

6. PROBLEMS ENCOUNTERED

The overall results of the NCCC test campaign met or exceeded the project objectives and goals. However, during the test campaign, we noted that some improvements can be made to module design, pressure vessel design, and to the potted fiber element; these will significantly improve the overall module performance for longer-duration testing. The following is the list of action items that need to be addressed in future test campaigns for breakthrough results and further advancement of the technology.

1. *Module design*: Tube sheet module design was a very good approach for scaling up the module size. This design allowed stacking of (5/8-in) bundles individually for fabricating 4-in modules. One of the issues we observed was epoxy delamination from the steel casing in long-term testing with multiple pressure and temperature cycling. We plan to redesign the potting mold and stop using metal in the mold.

2. *Gas bypass*: In the 4-in pressure vessels, the inlet gas entered the chamber from the top side port and left from the bottom side-port in the opposite end. Although this design is simple and makes testing and assembly easy, it does have the drawback of some gas bypass, which reduces the efficiency of the membrane module. To address this problem, we plan to design an insert that will block the direct gas path between inlet and outlet ports.

3. *Gas Flow Meters*: In the original design of the skid, we used thermal mass flow meters to measure the gas flows of, inlet, permeate, and retentate. However, we found that thermal mass flow meters are extremely sensitive to the gas composition changes, specifically to the hydrogen composition change, and become unreliable in the various mixed-gas composition environments. To address this issue, we purchased and installed a Coriolis flow meter on the retentate flow and used measured gas compositions to calculate volumetric flow rates. We need an additional Coriolis meter on the inlet flow so that flow measurements can be made more accurately and quickly.

4. *Syngas Feed Regulator (NCCC side):* The performance of the syngas regulator degraded during the 30-day test period. We suspect this could be due to particles trapped in the regulator diaphragm. We propose to install an upstream filter to avoid any particles entering the regulator.

5. *CO_2 Regulator (NCCC side):* The CO_2 regulator heater failed during the doped syngas testing runs and hindered the planned tests at higher CO_2 flow rates. At higher CO_2 flows, the regulator and the lines begin to freeze because the gas pressure was reduced at the regulator from the ~ 1000 psi delivery pressure to the operating pressure of the skid. This issue needs to be addressed and a properly rated heater must be installed in the CO_2 line.

6. H_2 Mass Flow Controller: The H_2 mass flow controller was too sensitive to the pressure differential across the controller and thus extra care was required when performing

parametric testing with varying pressure. We believe this was due to the incorrect C_v of the controller, and this must be checked before another test campaign.

7. *Skid Insulation*: The current insulation of pressure vessels and piping of the skid was not intended for long-term outdoor operations, and it was installed because of budgetary constraints. The skid must be properly insulated before the next test campaign. Also, heat trace wrapping on vessel #2 must be adjusted for efficient heating.

8. *Gas Analysis*: We were using only one gas chromatograph system for all gas measurements and were switching the gas sampling between the inlet, retentate, and the permeate. It does take considerable amount of time to flush the lines and get stable data as the sampling lines are long. It is preferable to have a dedicated gas chromatograph (GC) for each sample line; this would significantly reduce the test time and improve availability of data for parametric testing. Permeate and retentate sampling lines pressures are low, and thus it is preferable to have a pressure booster sampling pump to reduce the sampling line flush time. The inlet sampling location should also be relocated to be upstream of inlet flow meter such that the sampling valve can be left open all of the time so the flow is not counted in the inlet flow measurement.

9. *Alarms*: The SRI PBI test skid had provisions for providing updates on its alarm status to the NCCC. However, the alarm was not electrically connected during the test campaign; thus, the NCCC control system did not have any feedback on the status of the SRI skid operation. Because of this, we were not able to run the doped syngas tests overnight unattended. This must be addressed for future test campaigns.

10. *Gasifier Offsets*: If the gasifier is tripped, syngas flow is supposed to be automatically replaced with nitrogen to avoid pressure and flow fluctuations in the downstream. During the test period, the gasifier was tripped a few times and the syngas flow was replaced with nitrogen; this caused no issues with the PBI skid even though there was a sudden feed gas change from syngas to nitrogen and membrane modules recovered very well under gasifier trip conditions (Figure 9) reverting rapidly back to their original performance once the gasifier returned to normal operation. However, at one time when the PBI skid was in operation with syngas + hydrogen doping, the syngas flow ceased without the replacement nitrogen flow. At that time, we observed a sudden temperature surge in membrane modules. Sudden temperature changes impart very high stresses on the fiber bundle potting and sealing areas because these are made of materials with different thermal expansion coefficients and heat capacities and are prone to causing failure of modules. To prevent temperature spikes, the alarm conditions of the control program must be properly set so appropriate actions are taken.

11. *Fiber Morphology*: SRI just started investigating the effect of syngas exposure to the fiber morphology, and our preliminary investigation viewing the high-magnification pictures of the fiber bulk and the surface indicates the bulk structure remains unchanged after a 500-hr exposure to syngas. However, there were some deposits of materials on the surface and these are currently being analyzed. We will give our findings in a future report.

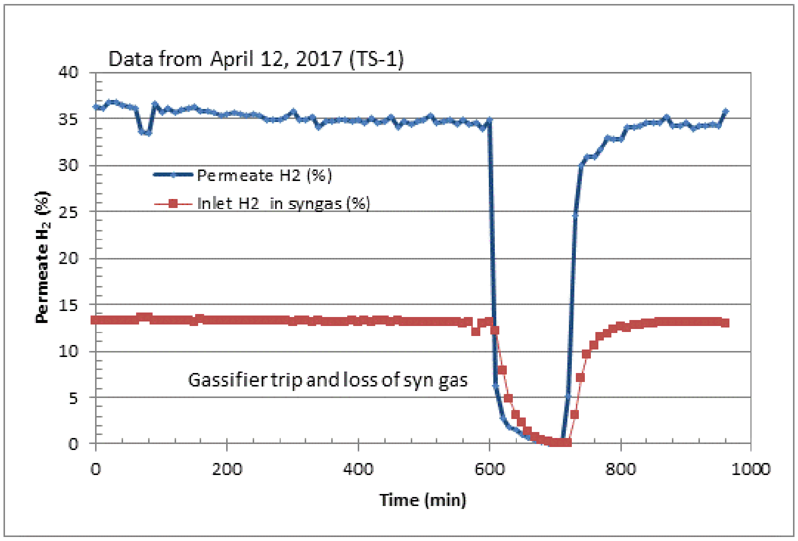

Figure 9. TS-1 module performance on April 12.

7. CONCLUSIONS AND LESSONS LEARNED

Summary: During the G5 gasifier run, SRI operated the PBI membrane skid continuously for more than 600 hr. During this time, most of the system components were at 200˚C and the valves and the control devices performed as designed. The TS-1 module was tested for about 500 hr with syngas and with syngas doped with H_2 and CO_2, and the TS-2 module was tested for about 48 hr. With syngas alone, the TS-1 module showed a greater than 3-fold H_2 stream enrichment while the CO_2 permeation remained unchanged or decreased slightly. The current testing confirms that greater than 90% recovery of CO_2 is possible at higher operating temperature (> 190˚C). In the future, we plan to conduct a longer run campaign with GEN 2 modules to evaluate the stability of epoxy fiber potting at higher temperatures.

Lesson Learned:

(1) Two of the modules that were shipped installed with the skid were damaged during shipping; as such, it is advisable to ship the modules separately.

(2) Since we planned well in advance and our work experience with the NCCC staff spanned more than two years, we were able to operate the skid over the complete window of gasifier operation time.

(3) Analytical issues: The skid-mounted gas analyzer failed to provide accurate measurements because it was prone to interference from minor constituents in syngas. The staff at the NCCC immediately made an NCCC gas analyzer available, and it was extremely accurate for monitoring the stream composition from the SRI skid. Next time, SRI plan to provide advance notice to NCCC requesting access to monitoring more than one streams.