DEMONSTRATION OF PILOT-SCALE HYDROGEN AND CO_2 SEPARATION MEMBRANE TECHNOLOGY ON WYOMING COAL-DERIVED SYNGAS

Final Executive Summary Report

Prepared for:

Diana Hulme

School of Energy Resources
University of Wyoming
Department 3012, 1000 East University Avenue
Laramie, WY 82071

Fund: 19911
Contract No.: 1217-20814 (EERC)

Prepared by:

Joshua J. Stanislowski
Scott G. Tolbert
Tyler J. Curran
Michael L. Swanson

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

2016-EERC-01-02 January 2016

DEMONSTRATION OF PILOT-SCALE HYDROGEN AND CO_2 SEPARATION MEMBRANE TECHNOLOGY ON WYOMING COAL-DERIVED SYNGAS

EXECUTIVE SUMMARY

In order to facilitate the use of hydrogen in integrated gasification combined-cycle (IGCC) applications or as a transportation fuel, hydrogen-from-coal technologies that are capable of managing carbon will be needed. Many technologies are under development for the separation of hydrogen from coal-derived syngas, and among the most promising are hydrogen separation membranes. Studies indicate a significant IGCC plant efficiency increase can be realized if warm-gas cleanup and hydrogen separation membranes are used in the place of conventional technologies. These membranes provide the potential to produce hydrogen while simultaneously separating carbon dioxide at system pressure. Membrane development activities need to take into account the impact of coal-derived impurities. Gasification syngas typically has many impurities that, if not removed, will poison most hydrogen separation materials. In order to commercialize this promising technology, scale-up to bench- and pilot-scale gasifiers is required so that the impact of impurities can be evaluated.

The work at the Energy & Environmental Research Center (EERC) focused on the testing of Praxair's hydrogen separation membrane for purifying hydrogen from coal-derived syngas. Praxair provided a pilot-scale membrane that was tested on syngas produced in the EERC's pilot-scale transport reactor development unit (TRDU). The goal of the project was to conduct a pilot-scale demonstration of coal-to-hydrogen production technology using warm-gas cleanup techniques and Praxair's hydrogen separation membrane. Four separate tasks were performed to enable the demonstration of the technology. Tasks 1 and 2 consisted of membrane acquisition and installation and making modifications to the TRDU and warm-gas cleanup systems to facilitate

the test runs. The testing occurred in Task 3, and the data derived were used to support Praxair's efforts in developing a techno-economic analysis and a modeling effort performed by the EERC in Task 4 of the project.

Approximately 470 hours of operation was completed on the TRDU gasifier, and over 260 hours of operation was conducted on the membrane. In spite of being a newly installed system, the water–gas shift (WGS) reactor, syngas compressor, and sulfur removal beds operated relatively well during the testing. Challenges with the candle filter periodically interupted operation of the membrane, but ultimately, the originally proposed testing goals were met.

Coal from the Antelope Mine in Wyoming was successfully gasified for the majority of the test campaign. Hydrogen concentrations leaving the gasifier were as high as 15% and were further increased to 20% on a dry basis after the WGS reactor. It was determined that operation of the sour shift catalyst near 400°C provided the highest level of shift when a low-sulfur coal was fired, and CO was able to be reduced below 1%. Periodic additions of hydrogen were able to push the hydrogen concentration to over 25% on a wet basis for specific tests. High-sodium Freedom lignite from North Dakota was also tested on the unit, and it was found that the fuel could be fired successfully with the addition of kaolin as a sodium-gettering agent.

The regenerable RVS-1 sulfur sorbent was shown to be able to reduce sulfur concentrations from nearly 4000 to below 5 ppm in one reactor. The sorbent was regenerated with oxygen, and sulfur levels returned to below 5 ppm at the reactor exit. Sulfur levels were typically below 1 ppm when the Antelope coal was fired and were in the 1–4-ppm range when test the North Dakota lignite was tested.

A hot-side sygnas compressor was successfully demonstrated to raise the pressure of the syngas from 120 to over 450 psi while maintaining the temperature above 450°F. This enabled the

test system to operate similarly to a commercial demonstration by maintaining the moisure, tars, ammonia, and chlorine in the syngas feed to the membrane. The membrane was exposed to a wide variety of contaminants found in syngas.

The membrane was operated on syngas over two separate test campaings. Initial flux on the membrane was lower than expected during the first campaign, but the flux did not significantly deteriorate through the test campaign. A bottle gas test was performed at the end of the campaign to see if higher hydrogen partial pressure would improve flux, but no signficnat improvement was noted. The system was dissassembled after the first campaign, and the membrane tubes were changed out with backup tubes. One tube failure was noted, but it was believed to have occurred during dissassembly of the vessel, since no process data indicated there had been a failure. The tubes were sent to Praxair for further analysis.

The second set of tubes was tested during the second campaign on both Antelope Powder River Basin coal and North Dakota lignite. The testing started with a bottle gas test, but lower-than-expected flux numbers were still observed. Significant parametrics were performed during the second campaign, and correlations for flux and permeance versus temperature, pressure, and flow were reported. As expected, the membrane flux was maximized when the highest partial pressure of hydrogen was delivered to the system at high flow conditions and 425°C. Membrane performance did not appear to signficantly change with time during the second campaign.

A bottle gas test was performed at the conclusion of the campaign to determine if the flux levels would return to the levels observed at Praxair if no contaminants were included in feed stream. A 1-hour test followed by an 8-hour hydrogen soak and an additional 1-hour test were performed. The permeance of the membrane improved slightly during the bottle gas tests, but the

performance did not return to the levels that were observed at Praxair. The tubes were removed at the conclusion of the testing and sent to Praxair for analysis.

Initial designs and data have been developed for a modular membrane technology that could be easily scaled up for a demonstration test. Prior to moving on to scale-up, the root cause of the low flux numbers needs to be determined. If there is found to be sulfur on the surface of the membrane, a polishing bed could easily be installed to remove sulfur down to a few parts per billion in the gas stream, thereby alleviating any sulfur issues. Available control methods for other syngas contaminants could also be inhibiting flux. Ideally, warm contaminant removal technologies would need to be used in order to take advantage of the thermal efficiency benefits provided by hydrogen separation membranes.

Two high-level assumptions were made in the present modeling effort that will significantly impact the overall plant performance if the criteria cannot be met. The first assumption was that the TRDU gasifier can achieve 1% methane concentration at the exit from optimization of operating temperature and process conditions. The second assumption was that membrane operation was optimized for an IGCC setting and that 95% hydrogen recovery could be achieved with a countercurrent nitrogen sweep. The necessity of the first assumption shows that the TRDU gasifier is probably not the best choice of systems for a hydrogen separation membrane. An entrained-flow gasifier does not produce significant amounts of methane and would likely be a better choice. Additionally, an entrained-flow system would likely be operated at higher pressure, providing additional performance benefits to the membrane. Overall, if these assumptions can be met, hydrogen separation membranes have the potential to significantly improve the efficiency of an IGCC system with CO_2 capture over conventional technology.