DEMONSTRATION OF HYDROGEN PRODUCTION FROM WYOMING COAL

Final Report

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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 CO_2 at system pressure. Membrane development to date has primarily occurred on bottle-derived syngas, and the impact of coal-derived impurities is unknown. 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 Energy & Environmental Research Center (EERC) together with the U.S. Department of Energy's (DOE's) National Energy Technology Laboratory and the State of Wyoming has completed a project to evaluate the performance of hydrogen separation membranes on coal-derived syngas. EERC small pilot-scale gasifiers were used to produce the syngas, and solid sorbents were used for warm-gas cleanup and water–gas shift (WGS). Three hydrogen separation membranes were exposed to coal-derived syngas for several hundred hours. This report details the results of the gasification, warm-gas cleanup, and membrane tests. An economic analysis is also presented that provides insights into the potential economic advantages of hydrogen separation membranes over conventional low-temperature technologies.

Three hydrogen separation membranes were exposed to coal-derived syngas for a total of 831 membrane-hours of exposure time. The syngas was produced from a Powder River Basin coal from the Antelope Mine in Wyoming using the small pilot-scale fluid-bed gasifier (FBG) and entrained-flow gasifier (EFG) at the EERC. Particulate was removed with a hot-gas filter vessel, and solid sorbents were used to remove contaminants such as sulfur, chlorine, and mercury. Both high-temperature and low-temperature WGS catalysts were used to maximize the hydrogen content of the syngas and minimize CO concentration. A membrane skid was built that was capable of exposing one membrane to the full-stream syngas and two slipstream membranes to syngas simultaneously.

The syngas produced for testing ranged from about 25% to 40% hydrogen on a dry basis. The concentration of hydrogen was lower than desired, but this was necessary to ensure consistent operation of the gasifiers. CO concentration was typically 2.5% or less for the duration of the tests. H_2S was removed from the gas stream using a two-stage sulfur sorbent system and was below 1 ppm for the test campaign. A chlorine guard bed was used to capture chlorine, and mercury sorbent was used to limit mercury exposure to the membranes. Other contaminants such as NH_3, HCN, and trace metals were monitored throughout the test run.

The first week of operation was performed on the FBG with each of the membranes online. The second and third weeks were performed on the EFG, but operational issues resulted in only 1 week of successful testing. Weeks 4–6 were performed on the FBG with the intent to run the gasifier at 200, 300, and 500 psi operating pressure. The 500 psi test run was moved back to 200 psi because of leaks that developed in the membranes.

The full-stream membrane had very high hydrogen purity and good flux and recovery rates through the first few weeks of testing. Hydrogen purity was at least 99.99% through the first few

weeks, and hydrogen recovery rates approached 50%. Hydrogen recovery would have been improved with increased partial pressure differential, but only 56 psi differential was achieved during the test run. Theoretical calculations with Sievert's law indicate that with a partial pressure differential of 100 psi, flux rates of 21.4 scfh/ft^2 may have been achieved. This falls well below the DOE 2010 goal of 200 scfh/ft^2. The highest flux was achieved during the earlier runs, despite the fact that partial pressure differential was higher for some of the membrane test runs later in the campaign. Also, a leak developed later in the test campaign that should have worked to increase flux for two reasons: 1) hydrogen was bypassing the membrane and penetrating to the permeate side through the leak and 2) the other syngas components leaking through the membrane acted as a sweep gas to increase partial pressure differential across the membrane. Even with the leak and the increased partial pressure, flux was decreased from where it was earlier in the test campaign. This indicates that there may have been some performance degradation because of syngas contaminants, but more investigation would be necessary to verify.

Slipstream Membrane 1 had good purity measurements, with readings up to 99.2% pure. Apparent flux rates were low initially until it was determined that the gas meter used to measure permeate flow was oversized. A low-range flowmeter was used starting in Week 4 testing, and it was determined that flux rates through the membrane were significant, even though the hydrogen recovery rates were low. Based on the Sievert's law calculation, the membrane was capable of achieving flux rates of 117 scfh/ft^2. Higher rates were achieved during the last week of testing, but the membrane was also shown to have a small leak. It was difficult to determine if any performance degradation occurred for Slipstream Membrane 1 because of the small leak that developed later in the tests and the lack of good flow measurements early in the test.

Slipstream Membrane 2 seemed to have very low flux rates during the initial stages of the program because the gas meter was not capable of measuring the permeate flow rate and hydrogen purity was low. Once the low-flow flowmeter was brought online, flux measurements were shown to improve, but maximum hydrogen purity reached was about 60%. Theoretical flux rates calculated at 100 psi partial pressure differential were as high as 29.4 scfh, but this was also with 60% hydrogen purity. It was difficult to determine if any performance degradation occurred for Slipstream Membrane 2 because of the lack of good flow measurements for most of the testing and a leak that appeared to be present for the duration of the test campaign.

Overall, the membranes were shown to meet some of the DOE's targets for hydrogen separation membrane development. Table ES-1 compares each of the membranes to the DOE performance goals. The data are based solely on the evaluations performed in this project and do not consider other testing that has occurred on the membrane material. All three membranes were below the 2010 target for flux rates, although Slipstream Membrane 1 came the closest to hitting 200 scfh/ft^2. All three membranes were operated below the 2015 target temperature. Sulfur tolerance was not able to be specifically determined as part of this test campaign, because sulfur was kept well below 1 ppm for the duration of the testing. Undoubtedly, small levels of sulfur reached the membranes, and they will be evaluated for sulfur poisoning in the post mortem analysis that is being conducted by the providers. Cost of the small separators is also not relevant to a commercial-scale operation, and cost numbers were not provided by the membrane producers. The membranes did not appear to provide significant WGS activity, but this was difficult to determine in this test program because in order to achieve the highest possible partial pressure differential, the syngas was shifted as far as possible before hydrogen separation. The

Table ES-1. Membrane Performance in This Test Campaign vs. DOE Targets

Performance Criteria	Units	2010 Target	2015 Target	Full-Stream Membrane	Slipstream Membrane 1	Slipstream Membrane 2
Flux (100 psi dP basis)	$ft^3/(hour*ft^2)$	200	300	21.3	117	29.4
Temperature	°F	572–1112	482–932	650	750	900
S Tolerance	ppmv	20	>100	Not determined (ND)	ND	ND
Cost	$\$/ft^2$	100	<100	ND	ND	ND
WGS Activity	–	Yes	Yes	ND	ND	ND
ΔP Operating Capability	psi	Up to 400	Up to 800 to 1000	600	300	200
Carbon Monoxide Tolerance	–	Yes	Yes	Yes	Yes	Yes
Hydrogen Purity	%	99.5%	99.99%	99.99	99.2	59.7
Stability/Durability	years	3	5	ND	ND	ND

Meets DOE 2015 goal.

Meets DOE 2010 goal.

Under DOE 2010 goal.

full-stream membrane met the 2010 goal for differential pressure operation capability according to the specifications, even though it was not tested that high in this program. The others were rated far below the specification. The membranes all appeared to have CO tolerance, since none of them completely deactivated with approximately 2% CO in the syngas during the test program. The full-stream membrane met the purity goal of 99.99% for the DOE 2015 target. Slipstream Membrane 1 came close to the DOE 2010 goal with 99.2% purity. Slipstream Membrane 2 probably had a significant leak and did not meet the purity goals.

A modeling study was undertaken to compare membrane processes to conventional CO_2 capture processes such as Selexol®. Aspen Plus was used as the primary modeling tool to determine the mass and energy balance around the process alternatives and, ultimately, the process efficiency. It was shown that with advanced process schemes, an additional 33 MW of power could theoretically be recovered from a 500-MW power system because of increased process efficiencies. This estimate likely represents the theoretical maximum gain and does not

take into account some of the potential losses that may be incurred with a commercial-scale hydrogen separation membrane system.

The DOE lists a 5-year membrane life as the durability target for 2015. It is difficult to derive the full life of the membranes over the duration tested. The leaks developed are certainly a concern, but likely easily resolved with additional engineering. The full-stream membrane exhibited what appeared to be a slight degradation in performance over the 331 hours of exposure time, although the exact degradation in performance was difficult to quantify fully because of the leak. More exposure time would necessary to determine the full potential impact of impurities. The testing did show that the membrane could still produce significant flux over several hundred hours of operation using commercial or near-commercial technologies for warm-gas cleanup. This is a promising result as future membrane materials are developed. There was no conclusive reduction in flux for Slipstream Membrane 1, which is also a promising result. Overall, it is difficult to exactly determine the life of a membrane based on these data, but no significant "showstoppers" were discovered as a result of exposure to coal-derived syngas.