HYDROGEN SEPARATION FOR CLEAN COAL APPLICATIONS

EXECUTIVE SUMMARY

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The two key technologies that could allow Wyoming coal to be used as the principal source of heat for carbon dioxide-free power generation are oxy-combustion and gasification. Oxy-combustion is the burning of coal in a carbon dioxide / oxygen mixture that eliminates nitrogen from the combustion process. Moving oxy-combustion forward at large scale depends on reducing oxygen production costs and redesign of power plants to operate within those more restrictive conditions. The gas product of oxy-combustion is primarily carbon dioxide, so the technology is sequestration friendly. Oxy-combustion is very much still in the development phase. The other approach, gasification, has been the center of much attention for the future of coal. Also dependent on oxygen production costs, gasification of Wyoming coal benefits from the ease with which sub-bituminous coal can be turned into synthesis gas: carbon monoxide and hydrogen. The synthesis gas can be used for liquid fuels production or chemical manufacture. If the coal gasifier is solely intended for power generation, then after gas cleanup and water gas shift processes, the gas composition can shifted to carbon dioxide and hydrogen. Separation of hydrogen from carbon dioxide is a critical technology to allow carbon sequestration. Although the net result is the same, hydrogen separation devices are more viable than carbon dioxide separation processes.

The objective of the project was to develop hydrogen separation technologies for coal gasification systems. The best technologies for hydrogen separation are hydrogen absorption systems and membranes. We wished to advance hydrogen membrane materials and build a bench scale system for high pressure hydrogen production using a ceramic based absorbent and a thermal cycling absorb/desorb process. WRI has identified these as the most appropriate technologies for the production of hydrogen from coal derived synthesis gas during previous work.

A facility was assembled first in which the rest of the work was conducted. The approach of the research project was to complete two parallel tracks in which hydrogen membranes and absorbent ceramic materials are produced at the same time that the thermal cycle hydrogen unit was designed and fabricated. Testing of the hydrogen adsorbing ceramic was iterative with ceramic development leading to scaled operations. The ceramic material was to come from a known class of materials, but required refinement to insure its suitability for the operational conditions. First as a powder, then as ceramic pieces, the material was adapted to fit the cycling bed system. The early tasks were designed to test the proof of concept for the combination of hydrogen absorbent and thermal cycling. Tests of the absorb / desorb process began with single variables and advanced to more complex performance testing with varying operational conditions. Membrane materials in several classes were also tested for hydrogen separation characteristics.

The thermal cycle process has been proven in its simplest configuration. Hydrogen will absorb and desorb into a sweep gas from appropriate sorbent pellets. A number of barium cerate based ceramic materials were prepared and tested for hydrogen absorbance characteristics. However the composition of the most likely hydrogen source gas, gasification syngas, creates too many issues with the original designed sorbent material. A new sorbent will be required for this technology to move forward.

The team has been successful in preparing 15 different amorphous alloy combinations for membranes which are thermally stable between 200˚C and 300˚C. The new membranes on porous stainless steel tubes can be easily incorporated into commercial devices.

Polymer membranes based on polyimides and polyamides have been successfully tested on porous stainless steel substrates in coal derived syngas for over 1000 hours and as hollow fiber bundles for 400 hours. The successes with hydrogen membrane materials and methods have expanded the research into other gas mixtures including carbon dioxide from coal derived combustion. Multiple palladium composite membranes have been successfully tested at several increasing scales. Membranes have survived 500 hour and 1000 hour tests in coal derived syngas and other gas mixtures with hydrogen flux values better than 2015 DOE targets in low carbon monoxide environments. The sensitivity of the flux to exposures below 100 ppm hydrogen sulfide was low.

We can make conclusions from the results of this project including the following:

- The thermal cycle absorption idea for delivery hydrogen at pressure seemed at first elegant and relatively straight forward. In retrospect the current class of hydrogen absorbent materials has characteristics that resist if not outright deny the operation of this process. The combination of the temperature regime where the materials are active and the thermodynamic processes that occur with mixed syngas products in this regime is problematic. We clearly learned what not to do. Current work with hydrogen storage materials may produce an alternative material that will not have the drawbacks found with the ceria based ceramics. If so the thermal cycle absorption process still has potential.

- Of the classes of hydrogen membrane materials tested, there remains a distribution of materials that run the range from ready to commercialize to needing significant work to develop reliable membranes. The amorphous alloys are at the very early development stage and remain a curiosity until proven reliable. Polymer based membranes are able to work at low temperatures, have modest hydrogen flux rates, but will not produce high purity hydrogen in a single pass. Composite palladium alloy membranes have the highest flux performance and hydrogen purity. Issues remain with the reproducible production of a large number of large scale composite membranes. Those issues are an example of the problems that arise moving from bench scale to manufacturing, and no one on the project has suggested that these are anything but normal and solvable bumps in the road.

We can make the following recommendations:

- The idea of a national hydrogen economy continues to change. Eight years ago the US Department of Energy was very much behind the development of IGCC power plants, hydrogen storage and hydrogen fueled automobiles. The emphasis was on high purity hydrogen suitable for PEM fuel cells. Now the DOE has curtailed support for hydrogen development drastically and moved to emphasis on renewables and carbon sequestration and reuse. The market for hydrogen remains what it has been for some time. The biggest users of hydrogen remain the producers of ammonia and fertilizers, petroleum refineries, chemical producers and electronics manufacturers. Only for electronics do they require hydrogen of very high purity.

- Wyoming still has the best resources for producing commercial quantities of hydrogen for existing users: natural gas for reforming and coal for gasification. While liquid fuel producers will be the most likely industries to get plants operational within Wyoming in the next five years, those plants will be in a position to pursue hydrogen production where the finances warrant that investment. Local production of hydrogen for use in Wyoming refineries is feasible.

- Chart Energy and Chemicals, the engineering firm within this research team, remains committed to pursuing commercial development of hydrogen separation modules based on palladium composite membranes. Chart is a very conservative organization financially. They will only pursue a product if there is a known market and reliable profit. It is a positive indicator that Chart has potential clients lined up for hydrogen separation modules for the right price. The composite palladium membranes show the best potential for commercial development.