Novel Composite Membranes for Hydrogen Separation in Gasification Processes in Vision 21 Energy Plants

Quarterly Technical Progress Report

6/01/03-9/30/03

Michael Schwartz

October 2003

DE-FC26-01NT40973

ITN Energy Systems, Inc.

8130 Shaffer Parkway

Littleton, CO 80127

DISCLAIMER

ABSTRACT

ITN Energy Systems, along with its team members, the Idaho National Engineering and Environmental Laboratory, Nexant Consulting, Argonne National Laboratory and Praxair, propose to develop a novel composite membrane structure for hydrogen separation as a key technology module within the future "Vision 21" fossil fuel plants.

The ITN team is taking a novel approach to hydrogen separation membrane technology where fundamental engineering material development is fully integrated into fabrication designs; combining functionally graded materials, monolithic module concept and plasma spray manufacturing techniques.

The technology is based on the use of Ion Conducting Ceramic Membranes (ICCM) for the selective transport of hydrogen. The membranes are comprised of composites consisting of a proton conducting ceramic and a second metallic phase to promote electrical conductivity. Functional grading of the membrane components allows the fabrication of individual membrane layers of different materials, microstructures and functions directly into a monolithic module. Plasma spray techniques, common in industrial manufacturing, are well suited for fabricating ICCM hydrogen separation modules inexpensively, yielding compact membrane modules that are amenable to large scale, continuous manufacturing with low costs.

This program will develop and evaluate composite membranes and catalysts for hydrogen separation. Components of the monolithic modules will be fabricated by plasma spray processing. The engineering and economic characteristics of the proposed ICCM approach, including system integration issues, will also be assessed. This will result in a complete evaluation of the technical and economic feasibility of ICCM hydrogen separation for implementation within the "Vision 21" fossil fuel plant.

The ICCM hydrogen separation technology is targeted for use within the gasification module of the "Vision 21" fossil fuel plant. The high performance and low-cost manufacturing of the proposed technology will benefit the deployment of "Vision 21" fossil fuel plant processes by improving the energy efficiency, flexibility and environmental performance of these plants. Of particular importance is that this technology will also produce a stream of pure carbon dioxide. This allows facile sequestration or other use of this greenhouse gas. These features will benefit the U.S. in allowing for the continued use of domestic fossil fuels in a more energy efficient and environmentally acceptable manner.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

ITN Energy Systems, along with its team members, the Idaho National Engineering and Environmental Laboratory, Nexant Consulting, Argonne National Laboratory and Praxair, propose to develop a novel composite membrane structure for hydrogen separation as a key technology module within the future "Vision 21" fossil fuel plants.

The ITN team is taking a novel approach to hydrogen separation membrane technology where fundamental engineering material development is fully integrated into fabrication designs; combining functionally graded materials, monolithic module concept and plasma spray manufacturing techniques.

The technology is based on the use of Ion Conducting Ceramic Membranes (ICCM) for the selective transport of hydrogen. The membranes are comprised of composites consisting of a proton conducting ceramic and a second metallic phase to promote electrical conductivity. Functional grading of the membrane components allows the fabrication of individual membrane layers of different materials, microstructures and functions directly into a monolithic module. Plasma spray techniques, common in industrial manufacturing, are well suited for fabricating ICCM hydrogen separation modules inexpensively, yielding compact membrane modules that are amenable to large scale, continuous manufacturing with low costs.

This program will develop and evaluate composite membranes and catalysts for hydrogen separation. Components of the monolithic modules will be fabricated by plasma spray processing. The engineering and economic characteristics of the proposed ICCM approach, including system integration issues, will also be assessed. This will result in a complete evaluation of the technical and economic feasibility of ICCM hydrogen separation for implementation within the "Vision 21" fossil fuel plant.

The ICCM hydrogen separation technology is targeted for use within the gasification module of the "Vision 21" fossil fuel plant. The high performance and low-cost manufacturing of the proposed technology will benefit the deployment of "Vision 21" fossil fuel plant processes by improving the energy efficiency, flexibility and environmental performance of these plants. Of particular importance is that this technology will also produce a stream of pure carbon dioxide. This allows facile sequestration or other use of this greenhouse gas. These features will benefit the U.S. in allowing for the continued use of domestic fossil fuels in a more energy efficient and environmentally acceptable manner.

Specific work performed and accomplishments for this reporting period include:

- Evaluation of single-phase sintering aids to obtain dry-pressed membranes with lower porosity;
- Evaluation of a nickel-boron alloy in place of pure nickel as the electron conducting component of the cermet membrane;
- Demonstration of thin-film, thermally-sprayed membranes with a leak rate less than 0.5%;

- Demonstration of 200 hr stability of the thin-film membranes in a hydrogen atmosphere;
- Demonstration of stability towards thermal cycling of a thin-film, thermally-sprayed membrane;
- Demonstration of chemical stability of the membranes towards steam- and carbon-dioxide-containing atmospheres; and
- Development of process flow schemes incorporating the ITN hydrogen separation membrane as well as a benchmark process flow scheme which uses pressure swing adsorption as the separation technique.

1. INTRODUCTION

This report describes the work performed during the latest reporting period. During the previous reporting period, work was performed in all areas of the program. Specifically, additional pyrochlore compositions were synthesized. Second, thin-film membranes that had previously been fabricated by thermal spray were tested. Finally, work continued on the plant design.

During this reporting period, work continued in all the above areas. Specifically, additional novel proton conducting materials were fabricated and tested. Because of continuing issues with high porosity in the dry-pressed membranes, work was performed on potential sintering aids. Additional thin-film membranes have also been fabricated and tested with lower leak rates than had been observed previously. Finally, the plant design has continued with three potential process flow schemes that compare a non-membrane benchmark plant with two, membrane-based plants. These results will now be discussed.

2. EXPERIMENTAL

2.1 Task 2 - Membrane Materials Development and Evaluation

2.1.1 Experimental Apparatus

No major changes were made to the experimental apparatus during this reporting period.

2.1.2 Preparation of Pyrochlore Membrane Materials and Cermet Membranes

During the previous reporting period, ITN continued with the fabrication of both pyrochlore powders and cermet membranes from these powders. However, measuring the conductivity of these materials proved to be difficult due to high porosity. To overcome this problem, we began to investigate metal oxides as potential sintering agents. Sintering agents examined included SiO_2, MgO, BaO, Na_2O and Li_2O and were all obtained from commercial sources. These sintering agents were added to the ceramic powder as either the oxide or carbonate, as appropriate, and milled thoroughly. Membranes were prepared using the procedures discussed previously including maintaining a sintering temperature of 1420-1440 ^{o}C. However, none of these sintering aids were effective in reducing membrane porosity.

A second approach to reducing porosity was to use a nickel boron alloy in place of the nickel as the metallic component of the cermet membrane. The strategy here is that the alloy has a lower melting point than nickel, 1065 vs. 1453 ^{o}C, respectively, which would promote liquid phase sintering. Additionally, nickel boron alloys are known to have better wetting properties than metals towards metal oxides and this may cause stronger bonding, and higher density, than with the pure nickel.[1,2]

Membranes containing a nickel boron alloy in place of the nickel were fabricated using a nickel boron alloy of 15 wt% boron which was obtained commercially (Goodfellow). The membranes were prepared in a manner similar to the nickel-containing membranes with the exception that the sintering temperature was varied from 1000-1440 ^{o}C. Despite the use of the nickel boron alloy, membranes with acceptable density and low porosity were not obtained.

3. RESULTS AND DISCUSSION

3.1 Task 1 - Test Plan and Project Management

Regular teleconference calls were held between ITN and the Idaho National Engineering and Environmental Laboratory (INEEL) and ITN and Nexant and Praxair in order to direct work in this program. A meeting was held between ITN, Nexant and Department of Energy (DOE) representatives during the 20^{th} Annual International Pittsburgh Coal Conference. In addition, the Principal Investigator presented results of this work at the 20^{th} Annual International Pittsburgh Coal Conference. Finally, ITN has decided to pursue a patent based on the Invention Disclosure submitted during the previous reporting period. The patent application is in the process of being prepared.

3.2 Task 2 - Membrane Materials Development and Evaluation

3.2.1 Preparation and Characterizations of Pyrochlore Materials and Cermet Membranes

During the previous reporting period, screening of proton conducting ceramic materials was begun with conductivity as high as 0.02 S/cm obtained at 900 ^{o}C. During this reporting period, the bulk of the effort was focused on obtaining higher densities through the use of sintering aids and a nickel boron alloy. As noted above, we were unable to successfully obtain membranes with high density and low leakage rate. Because of this, we have adopted another strategy for solving this problem. Specifically, we will examine some nickel alloys with other metals. The reason for this is to obtain better wetting between the metal and ceramic phase by alloying the nickel with metals that are less reducible than nickel. Currently, liquid nickel de-wets from the ceramic and does not yield high density and low porosity membranes. By using a better wetting alloy, we expect no de-wetting which will result in higher sintered density. These experiments are currently underway and the results will be reported in the upcoming reporting period.

Experiments on membrane stability towards water and carbon dioxide were also performed during this reporting period. These experiments were performed on thermally-sprayed membranes fabricated at INEEL and the results are discussed below.

We are also measuring proton conductivity in wet atmospheres, in addition to dry atmospheres, in order to gain information as to the conduction process in these materials. Since protons can be introduced into the lattice through two different mechanisms, one dry and one involving humidity, this is an important measurement. To date, we have not collected enough data to be able to determine which mechanism is dominant but these measurements will continue.

3.3 Task 3 - Thin-Film Device Fabrication

During the previous reporting period, thermally-sprayed, thin-film membranes were fabricated with modified procedures and substrates in order to reduce the leak rate. During this reporting period, these membranes were tested and found to exhibit low leak rates, some less than 1%. These thin-film membranes were also tested for stability in water and carbon dioxide streams as well as thermal cycling. These results will now be described.

Figure 1 shows a plot of membrane conductivity as a function of operating time under H_2 and H_2/H_2O atmospheres as well as after one thermal cycle. The membrane consisted of ~40 wt% Ni and was ~500 µm thick. The results are all at 900 ^{o}C. As can be seen in the Figure, the conductivity of the sample was ~0.03 S/cm and was completely stable over the 200 hr experiment. Thermal cycling also had no effect on the membrane performance. Conductivity in a steam-containing atmosphere was higher than in the dry atmosphere, as expected for a proton conductor.

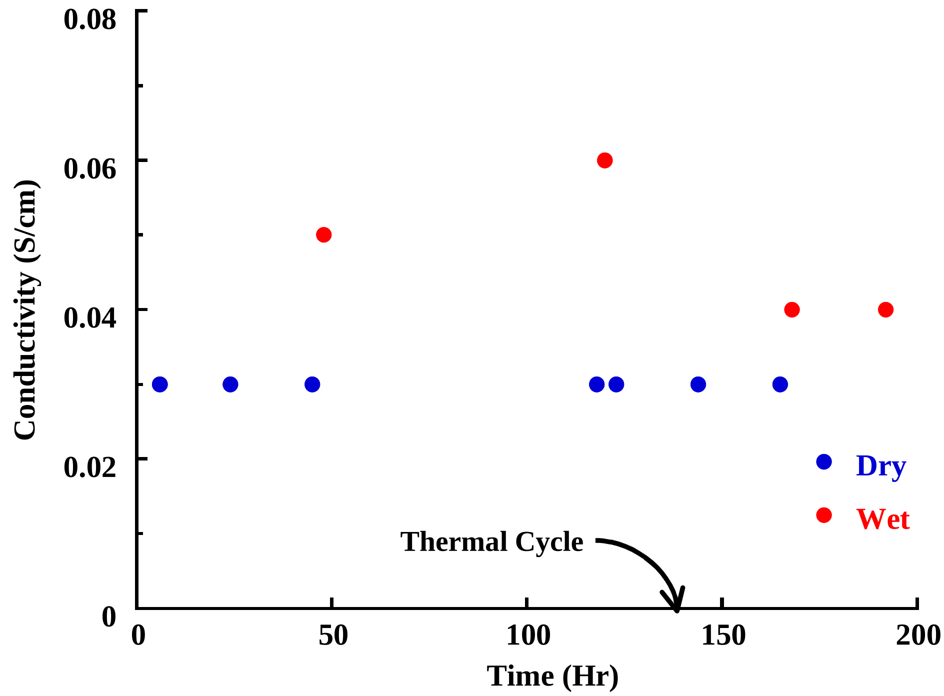


Figure 1. Plot of conductivity vs. time for a thermally-sprayed membrane at 900 ^{o}C. See text for the experimental details.

The effect of a CO_2-containing atmosphere, as well as the membrane leak rate, are shown in Figure 2. The data are reported as a thickness-normalized H_2 flux rate, rather than conductivity as in Figure 1, since we are not sure of the hydrogen concentration due to the reaction of the CO_2 with the H_2 to produce H_2O and CO in the reverse water-gas-shift reaction.

The data shown in Figure 2 show that the membrane is completely stable towards CO_2-containing atmospheres over the time tested. The membrane also showed a very low leak rate, ~0.5%, over the course of the experiment. Not only did the flux remained stable, but the leak rate as well, indicating that these pyrochlore proton-conducting materials will be stable under actual operating conditions.

A high surface area membrane, ~100 cm^2, was also prepared during this reporting period. A photograph of this membrane is shown in Figure 3. The membrane showed a high leak rate as it was prepared on a stainless steel substrate, rather than Ni, as Ni substrates were not available at the time of the experiment. The use of the stainless steel substrate required the use of stainless steel as the metal in the cermet membrane, rather than Ni. Ni tubular substrates have been ordered and membranes will be fabricated using these substrates in the upcoming reporting period.

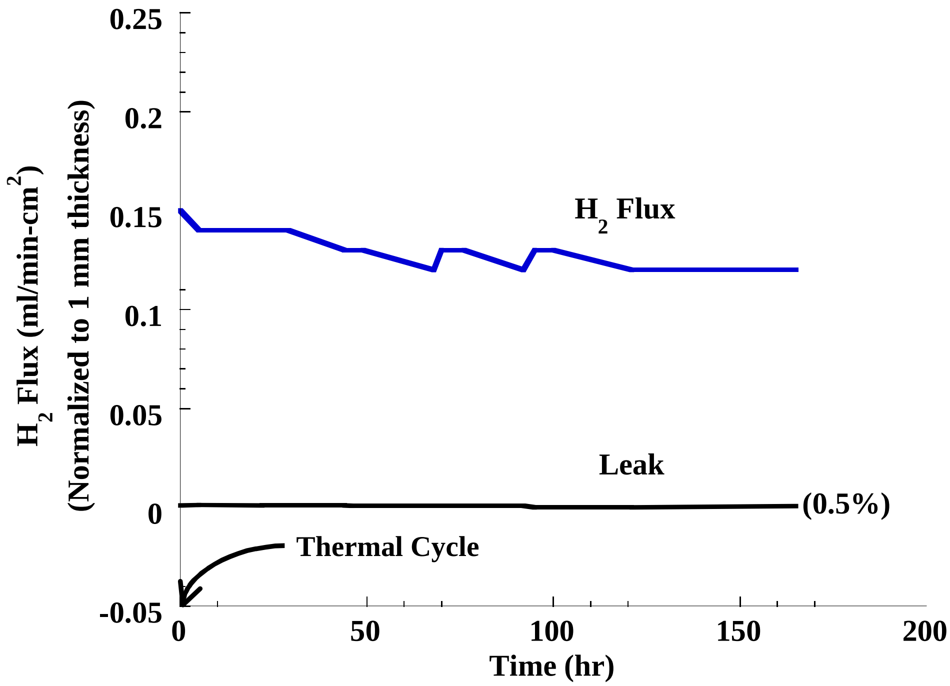


Figure 2. Plot of normalized H_2 flux rate as a function of time for a thermally-sprayed membrane in a CO_2-containing atmosphere at 900 ^oC. See text for experimental details.

Work in this Task will now focus on obtaining thinner membranes and scaling up the active surface, while maintaining high flux rates and low leak rates. Several parameters, including substrate surface preparation, powder morphology and thermal spray conditions will be evaluated.

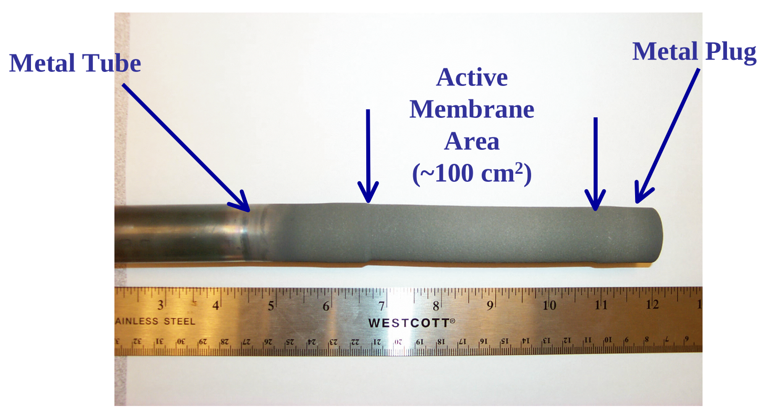


Figure 3. Photograph of a thermally-sprayed, high surface area membrane.

3.4 Task 4 - Engineering

In the previous reporting periods, Nexant, with input from Praxair and ITN, continued in refining the potential process flow diagrams for the Vision 21 plant according to DOE's "FutureGen" program specifications. Specifically, the plant design is based on a 275 MW single-train gasifier which produces approximately one million tons of carbon dioxide with the goal of sequestering 90% of this carbon dioxide. During this reporting period, work continued on refining these flow diagrams focusing on above specifications.

The first process scheme serves as a benchmark design and is shown in Figure 4. This design does not utilize a hydrogen separation membrane but rather a pressure swing adsorption (PSA) process for separating H_2 from CO_2.

Two additional process schemes were also developed in which the ITN membrane is used to separate the hydrogen, rather than PSA. These process flow schemes are shown in Figures 5 and 6. The difference between the two schemes is that one of the schemes (Figure 5) utilizes a conventional low temperature gas clean-up process while the second scheme (Figure 6) utilizes an advanced warm gas clean-up process. The warm gas clean-up components utilized in the latter process scheme are still under development and have not been commercially demonstrated.

4. CONCLUSIONS

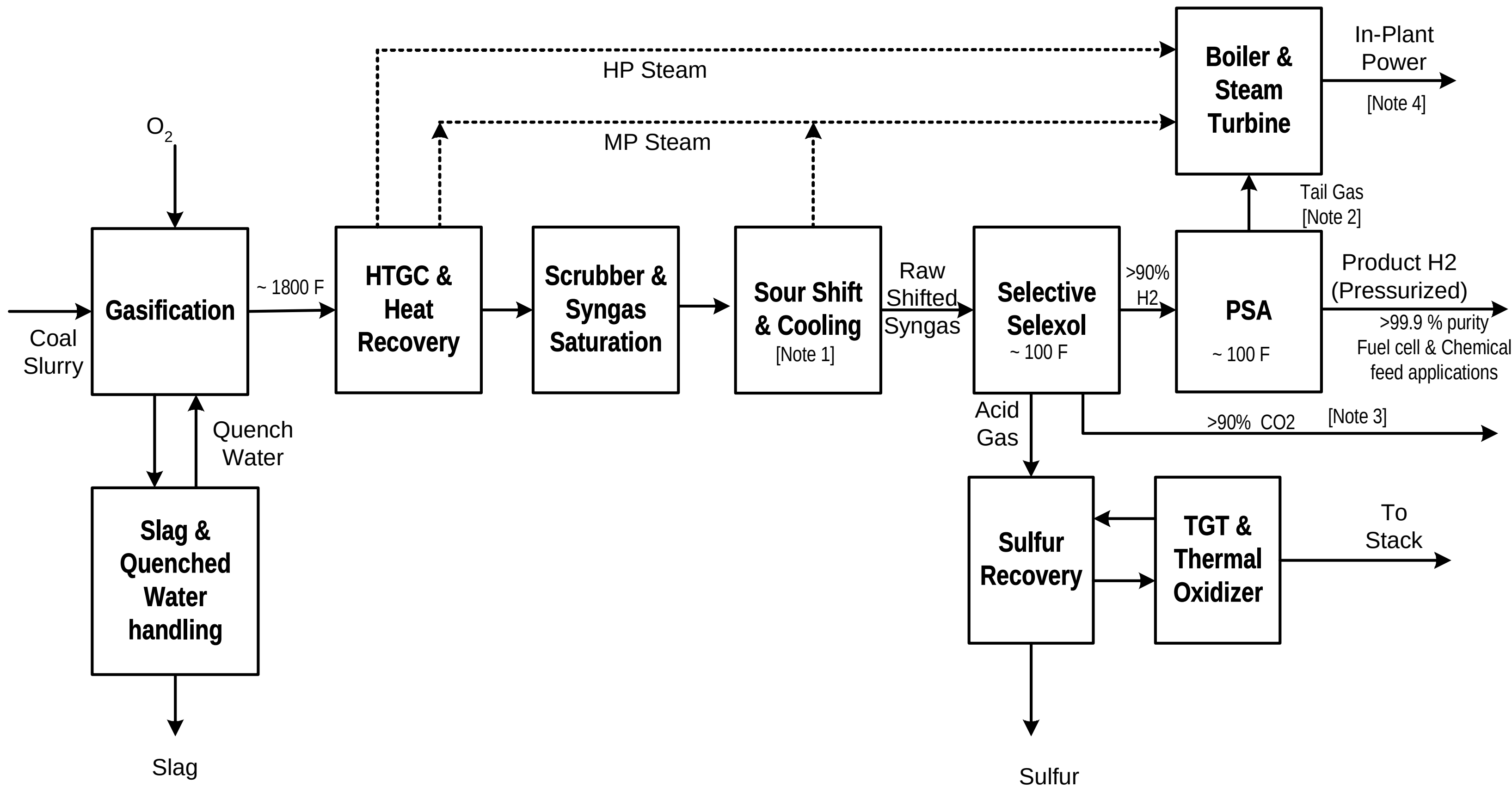
Work on this program is continuing in all areas. At ITN, work continued on fabricating and evaluating novel pyrochlore proton conducting materials. The major issue has been the difficulty in reproducibly fabricating dense membranes by dry-pressing. To this end, work will focus on using nickel alloys in place of nickel in order to prevent de-wetting of the metal from the ceramic.

In the area of thin-film fabrication, leakage through the membranes has been dramatically reduced with leakage rates below 1%. Thermally-sprayed membrane have also been shown to be stable when operated under steam and carbon-dioxide-containing atmospheres. Work will now focus on reducing the membrane thickness to 50 µm.

Finally, the design component of the program is continuing with the completion of three process flow schemes that account for the specifications of a “FutureGen” plant. Work will continue on putting more detail into the process flow schemes as well as in developing a more detailed model for the membrane.

5. REFERENCES

1. Y.M. Chow, W.M. Lau and Z.S. Karim, Surf. Interface Anal., 31, 321 (2001).
2. C.-T. Hu and W.-C. Chiou, Met. Mat. Trans. A, 32A, 407 (2001).



Note 1 - COS Hydrolysis included
Note 2 - Low pressure (~ 5 psig); need compression if send to a turbine
Note 3 - Contains CO, etc ready for sequestration but not vent to atmosphere
Note 4 - H2 is the primary product; power co-produce for in-plant us via BOP

Figure 4. Process flow scheme for a coal-gasification-based hydrogen and power co-production plant with CO_2 removal using PSA.

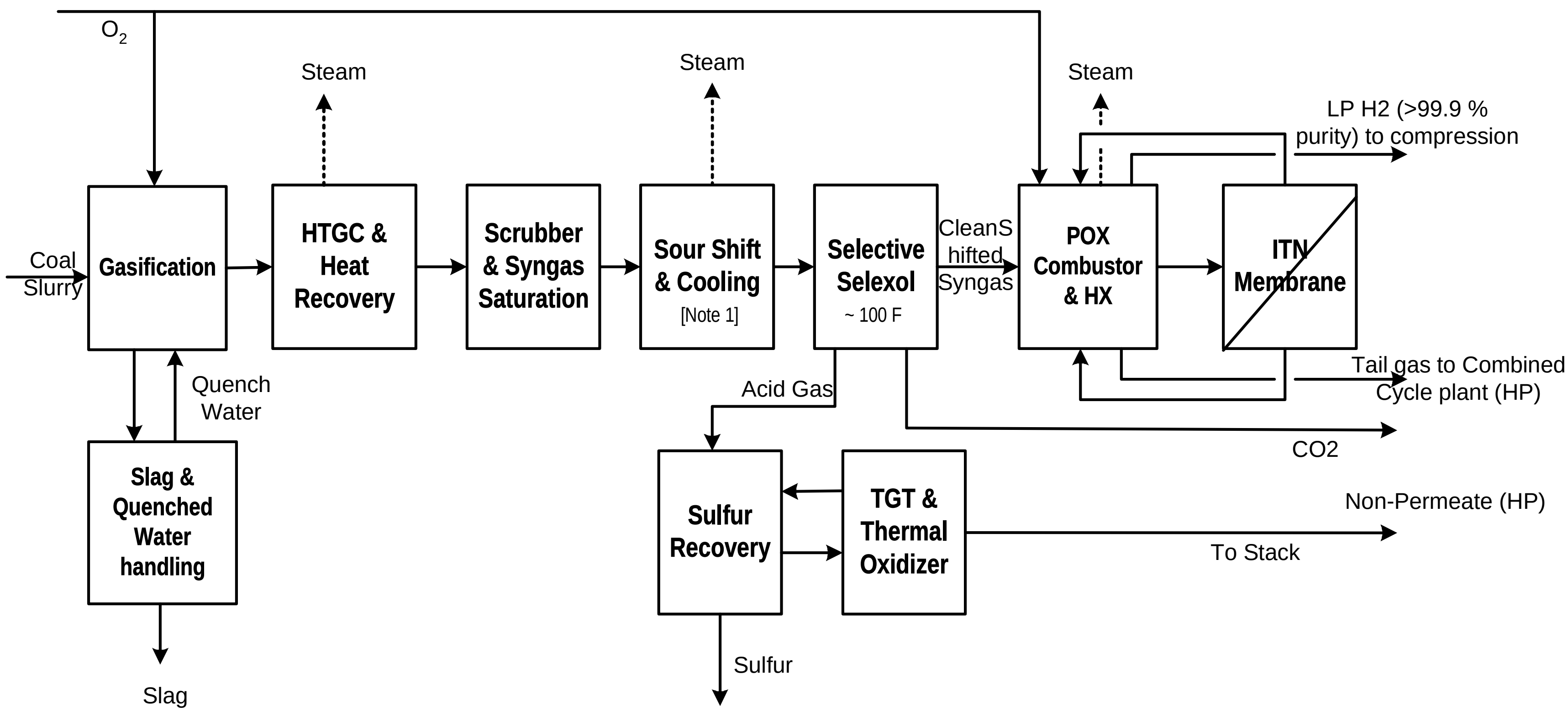
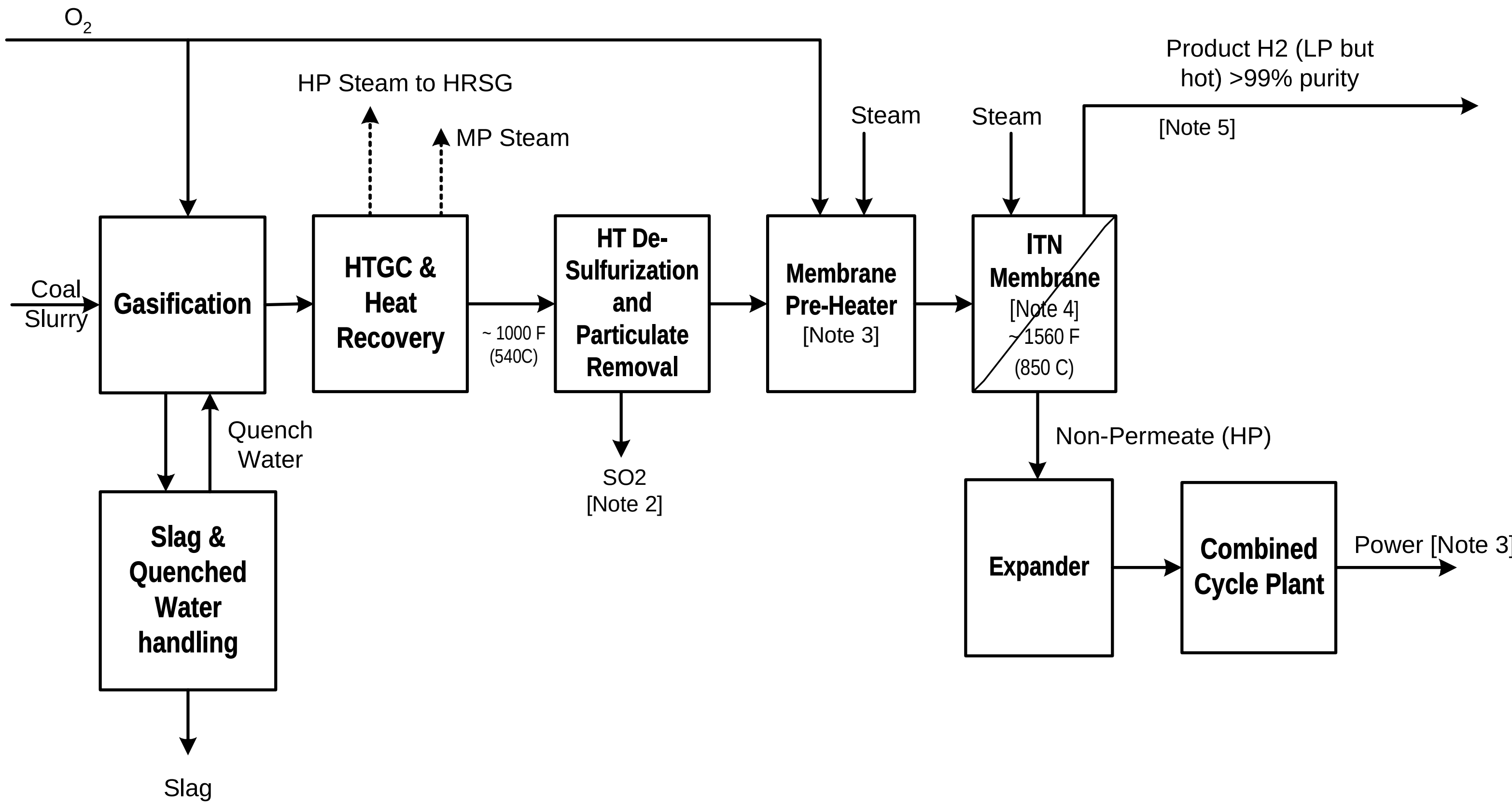


Figure 5. Process flow scheme for a coal-gasification-based hydrogen and power co-production plant with CO_2 removal using the ITN hydrogen separation membrane and low temperature gas clean-up.



Note 1 - Similar to Parson's conceptual design [Hydrogen Production Facilities Plant Performance and Cost Comparisons]
Note 2 - Metal oxides HT sorbents either fluidized-bed or moving-bed design followed by H_2SO_4 production
Note 3 - POX (Hydrogen Technology Inc.); Option is to use a fired heater but have to deal with emissions
Note 4 - Evaluate with and without WGS activity
Note 5 - Both the H2 and the Non-Permeate streams leaving the membrane are hot; recover heat via heat exchange

Figure 6. Process flow scheme for a coal-gasification-based hydrogen and power co-production plant with CO_2 removal using the ITN hydrogen separation membrane and warm temperature gas clean-up.