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**A Novel Membrane Reactor for Direct Hydrogen Production from Coal**

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## DISCLAIMER

**ABSTRACT**

Gas Technology Institute is developing a novel concept of membrane gasifier for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal synthesis gases. The objective of this project is to determine the technical and economic feasibility of this concept by screening, testing and identifying potential candidate membranes under high temperature, high pressure, and harsh environments of the coal gasification conditions. The best performing membranes will be selected for preliminary reactor design and cost estimates.

To evaluate the performances of the candidate membranes under the gasification conditions, a high temperature/high pressure hydrogen permeation unit will be constructed in this project. During this reporting period, the mechanical construction of the permeation unit was completed. Commissioning and shake down tests are being conducted. The unit is capable of operation at temperatures up to 1100$^{o}$C and pressures to 60 atm for evaluation of ceramic membranes such as mixed ionic conducting membrane. The membranes to be tested will be in disc form with a diameter of about 3 cm. Operation at these high temperatures and high hydrogen partial pressures will demonstrate commercially relevant hydrogen flux, 10~50 cc/min/cm$^2$, from the membranes made of the perovskite type of ceramic material.

Preliminary modeling was also performed for a tubular membrane reactor within a gasifier to estimate the required membrane area for a given gasification condition. The modeling results will be used to support the conceptual design of the membrane reactor.

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## INTRODUCTION

The objective of this project is to develop a novel membrane reactor for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal synthesis gases. This concept has the potential of significantly increasing the thermal efficiency of producing hydrogen and simplifying the processing steps thus reducing the cost of hydrogen production from coal. The specific objective of the project is to determine the technical and economic feasibility of using the membrane reactor to produce hydrogen from coal. GTI and our project team (University of Cincinnati, University of Florida and American Electric Power (AEP)) have identified and will evaluate potential membranes (ceramic and metal) suitable for high temperature, high pressure, and harsh coal gas environments. The best performing membranes will be selected for preliminary reactor design and cost estimates. The overall economics of hydrogen production from this new process will be assessed and compared with other hydrogen production technologies from coal.

Our approach to membrane material screening and testing is to first identify the materials that have good thermal stability at gasification temperatures. The candidate membranes will be evaluated for their hydrogen flux in a laboratory permeation unit. The laboratory data will provide the basis for a preliminary membrane gasifier design, process development and economic analysis. In the next stage of material screening, chemical stability of the membranes with the syngas and its contaminants generated from the coal gasification will be evaluated. The trade-off between the hydrogen permeability and chemical stability will be determined.

As coal gasification for hydrogen production occurs at temperatures above 900$^{o}$C and pressures above 20 atm, it is critically important to evaluate the hydrogen flux of the candidate membrane materials under these operation conditions. To this end, a high pressure/high temperature permeation unit is required. The unit is capable of operating at temperatures and pressures up to 1100$^{o}$C and 60 atm respectively. The unit will allow screening and testing of the membrane materials at more realistic gasification temperature and pressure conditions. Furthermore, the test unit will be able to demonstrate much higher hydrogen flux from the membranes than what is reported in the literature.

During this reporting period, the majority of effort was directed toward construction of the high pressure/high temperature permeation unit. Mechanical construction was completed. Commissioning and shake down tests are currently being performed. The task of conceptual membrane gasification reactor design was also initiated by developing a preliminary model for a tubular membrane reactor within a gasifier. This modeling activity is also described in this report.

## EXECUTIVE SUMMARY

The design challenge for the high pressure/high temperature permeation unit is mainly in the membrane sealing and the materials of construction for the cell. The high pressure sealing issue can be addressed by using a sweeping gas in the permeate side at a pressure nearly equal to the feed side. Proper sealing between the ceramic membrane and its supporting tube at high temperatures remains a challenge due to the different thermal expansion coefficients for the sealing material and the membrane. The pressure rating for materials of construction can be reduced if the pressures are balanced between the inside and the outside of the permeation cell, as in the current design for this project.

GTI has constructed a high temperature/high pressure permeation unit for measuring hydrogen flux through high temperature ceramic membranes. The unit was designed to operate at temperatures up to 1100$^{o}$C and pressures to 60 atm for evaluation of disc membranes with a diameter of about 3 cm. The permeation assembly consists of a tubular permeation cell, a surrounding cylindrical heater, and an enclosing pressure vessel. The membrane to be tested will be attached or cemented to the end of a holding tube. Hydrogen-containing gas is directed to the feed side of the membrane through another tube opposite to the membrane holding tube. Within the holding tube is another inner tube, where an inert gas is used to sweep the hydrogen permeate through the annular section between the membrane tube and the inner tube. The remaining non-permeate feed gas exists the system through an outer tube, which separates the heater from the membrane holding tube. Therefore, the pressure differential across the membrane will be minimal, which would make the membrane sealing less difficult.

The inner tube, outer tube and the membrane holding tube are made of Inconel for its good resistance to heat and easy machining and welding. The entire permeation cell assembly is heated by a cylindrical heater, which is enclosed in a pressure vessel purged with inert gas. The hydrogen content of the permeate, after cool down, will be analyzed by a GC to determine the hydrogen flux through the membrane.

Preliminary modeling work was also performed to support the conceptual design of the membrane gasification reactor. The model provides an estimate of the membrane area required for a given coal gasification condition. The hydrogen flux across the membrane depends on the difference of hydrogen partial pressures on the feed and the permeate side. However, the feed side hydrogen partial pressure is also affected by the rate of hydrogen generation from the chemical reactions in the gasifier. It was found that hydrogen production from the membrane gasifier could be limited by kinetics of the chemical reactions, water gas shift and reforming reactions, in the gasifier.

An industrial advisor meeting was held on March 2 at GTI. Representatives from ICCI (Illinois Clean Coal Institute), AEP (American Electric Power), Wah Chang (a Palladium membrane manufacturer), Schott Glass and ProTek Inc. (a high temperature membrane manufacturer representative) attended this meeting to discuss and review the project status.

A project kick-off meeting was held with the DOE program manager at DOE/NETL on March 4th.

## EXPERIMENTAL

Construction of the permeation unit was completed in this quarter. A photo of the unit is shown in Figure 1. The unit is enclosed within a walk-in hood. Two control panels were installed outside of the enclosure for easy monitoring and safe operating of the unit without the need of entering into the hood. Four Brooks mass flow controllers are installed for controlling and measuring the inlet gas flow rates. The exhaust gas is cooled down by two heat-exchanger coils using cooling water before venting out of the system. A back pressure regulator located at the system outlet is used to maintain the overall pressure. Two pressure relief valves were installed in the feed section to avoid over pressurizing the unit.

The permeation cell was mounted vertically on a support frame, which was bolted to the floor. The permeation cell mainly consists of a pressure body, a 5" schedule 80 pipe and two sets of 5" ANSI B16.5 Class 1500# flanges. This cell was fabricated by a local machine shop. Inside the permeation cell, there is a cylindrical ceramic heater made by Internal Ceramics & Heating System. Figure 2-(a) is a side view of the permeation cell showing the heater before it was assembled. Figure 2-(b) shows the heater electrical wires insulated with Teflon, which were connected to two feedthrough conductors located in the flange. Also shown in Figure 2-b is an Inconel tubing within the center of the heater. This tube separates the heater from another tube that holds the membrane disk, as shown in Figure 3. The membrane disk is attached to the open end of the tube in Figure 3. This tube will be inserted into the middle of the tube shown in Figure 2 (b).

Electrical wiring including heater connections was completed. The instrumentation and data acquisition system have been set up. Shake down tests are currently being conducted to ensure that the system is leak tight and reaches the rated temperature, 1100C. Initial permeation tests will be conducted for a $BaCe_{0.9}Nd_{0.1}O_{3-x}$ (BCN) or $BaCe_{0.9}Y_{0.1}O_{3-x}$ (BCY) perovskite membrane to establish baseline performances. These membranes have been prepared and are currently being tested in a low pressure permeation unit under a research project sponsored by the Illinois Clean Coal Institute. The low pressure permeation data will be extended to the high pressure region when the membranes are tested in the high pressure permeation unit.

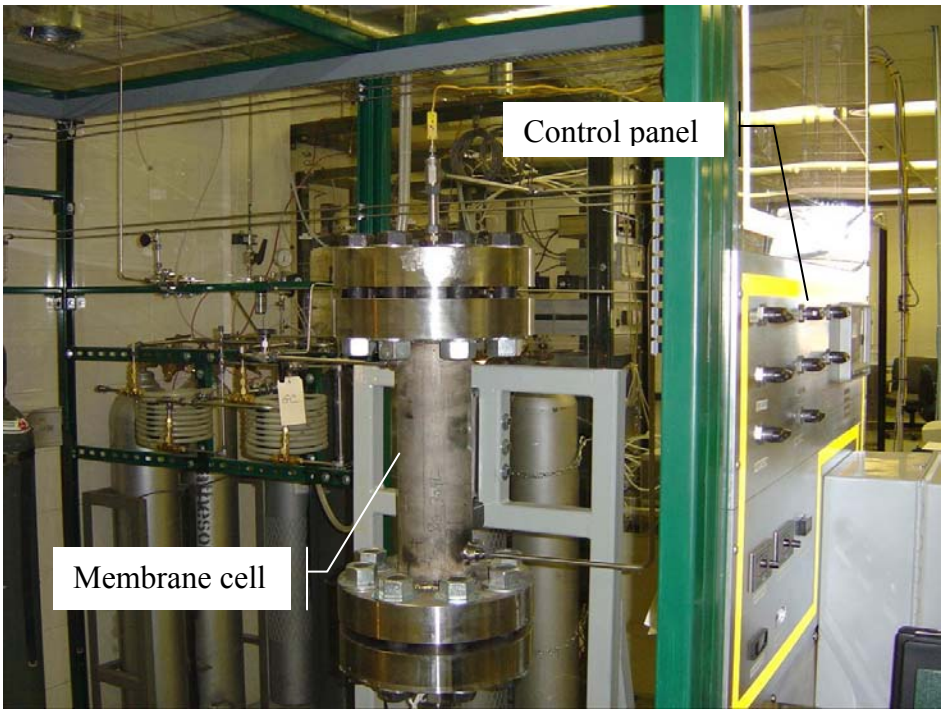


**Figure 1. High temperature/high pressure membrane permeation unit**

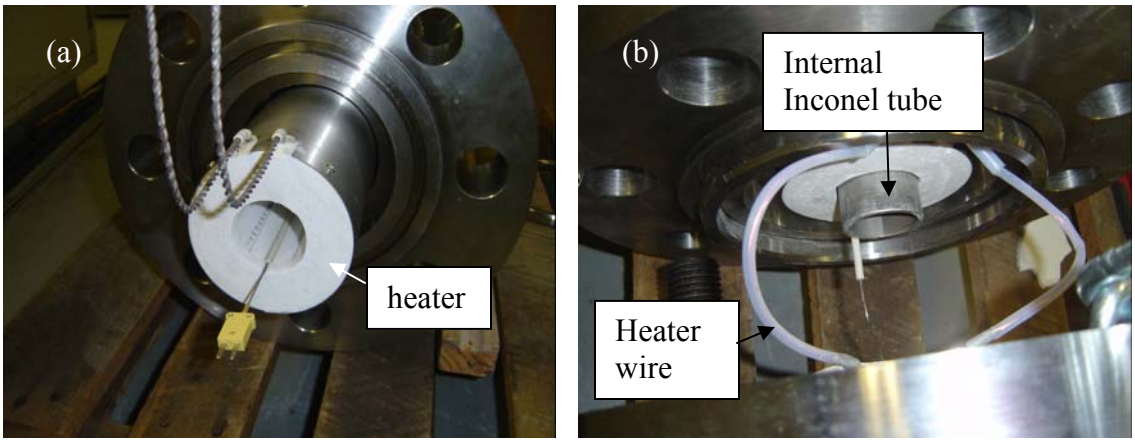


**Figure 2 Membrane permeation cell, (a) cylindrical ceramic heater, (b) heater wire connection and an internal Inconel tube**

**Figure 3. Membrane holding tube. The disk membrane will be attached to the end of this tube, which will be inserted into the center of the tube in Figure 2 (b)**

## MODELING OF MEMBRANE REACTOR

To support the conceptual design of the membrane gasification reactor, the required size or dimension of the membrane module for a given operating condition must be determined. A modeling approach is used for this task. Figure 4 is a conceptual diagram showing a section of tubular membrane within a gasifier. The gas phase reactions in a gasifier can be described by the following reactions [1]:

$$H_2O+CO = CO_2+H_2 \quad (1)$$

$$CH_4+CO_2 = 2CO+2H_2 \quad (2)$$

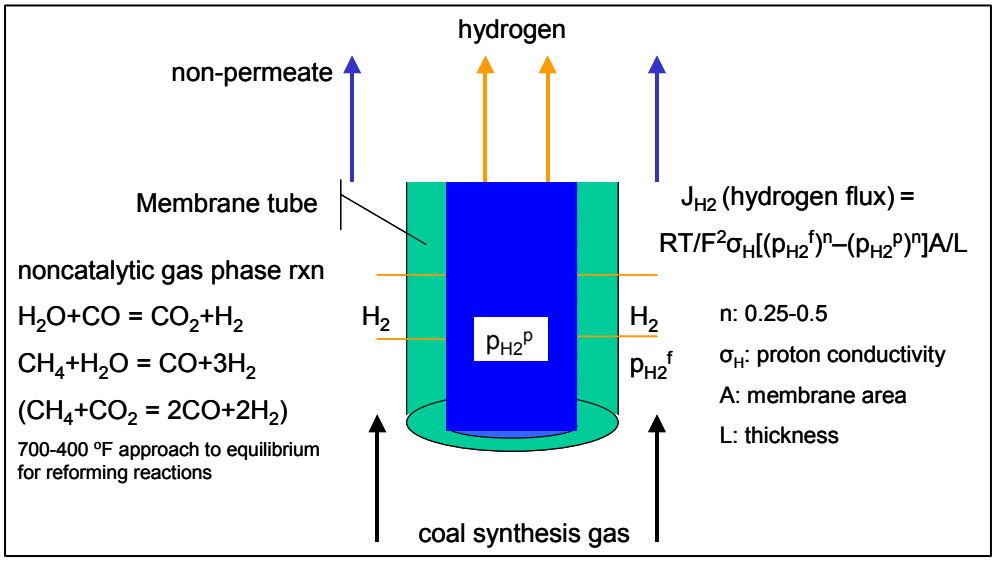


**Figure 4. Conceptual diagram for modeling of membrane reaction in a gasifier**

At steady state, the rate of hydrogen generation from the above reactions is equal to the permeation rate of hydrogen through the membrane, which generally can be expressed by the following simplified form for a proton conducting perovskite membrane [2]:

$J_{H2}$ (hydrogen flux) $= RT/F^2 \sigma_H [(p_{H2}f)^n - (p_{H2}p)^n] A/L$ (3)

where
R: gas constant
T: temperature
F: Faraday constant
$\sigma_H$: proton conductivity
$p_{H2}f$: hydrogen partial pressure at the feed side
$p_{H2}p$: hydrogen partial pressure at the permeate side
n: constant, 0.25-0.5
A: membrane area
L: membrane thickness

The removal of hydrogen from the system will promote more hydrogen generation from the gas phase reactions in the gasifier. However, the reaction rate has to be fast enough so that the hydrogen partial pressure in the feed side is higher than the permeate side for the hydrogen permeation to take place according to the above equation, Eq. (3). Because the reforming reactions without catalysts are expected to be very slow, their reaction rates under noncatalytic conditions need to be assessed. For the current initial modeling effort, an approach to equilibrium temperature of 400C for the reforming reaction, Eq. (2), was assumed at the entrance of the membrane tube and a 200C approach to the equilibrium at the exit of the membrane. For the shift reaction, Eq. (1), an approach to equilibrium temperature of 200C throughout the membrane length was assumed. The initial model developed will be used to assess the performance of the membrane reactor in the gasifier.

## RESULTS AND DISCUSSION

No experimental data have been collected during this reporting period.

The model developed for the membrane gasification reactor was used to simulate hydrogen production directly from a gasifier for Illinois #6 coal. The following conditions are assumed:

Coal feed rate: 1000 lb/hr
Steam/carbon ratio (mole): 1
Oxygen/carbon ratio (mole): 0.4
Tubular membrane diameter: 1 cm
Membrane length: 300 cm
Number of membrane tubes: 200
Proton conductivity of membrane: 0.1 S/cm
Membrane thickness: 0.001 cm
Gasifier temperature: 1950F
Gasifier pressure: 30 atm
Permeate pressure: 1.5 atm (hydrogen)

The overall hydrogen flux from the membrane was calculated by dividing the membrane length into five sections and integrating the flux equation, Eq. (3). While the hydrogen (partial) pressure on the permeate side, $p_{H2}p$, is kept at 1.5 atm, that of the feed side, $p_{H2}f$, is calculated based on the equilibrium conditions of the chemical reactions, Eq. (1) and (2) with certain approach temperatures as described above.

The simulation results are shown in Figure 5 for the hydrogen concentration and the hydrogen flux at different positions of the membrane. As can be seen, hydrogen permeation primarily takes place at the beginning section of the membrane tube, where the hydrogen mole fraction and its partial pressure across the membrane are high. The hydrogen mole fraction and permeation rate decrease toward the exit of the membrane tubes. The hydrogen mole fraction reaches a constant value of about 5%, where the partial pressures of hydrogen on both the feed and the permeate sides are about equal and hydrogen permeation can no longer proceed. This can be seen from the flux curve in Figure 5, where the hydrogen product gas flows from the membrane are almost zero after about 70% of the membrane length. This particular example shows that the membrane area is over sized.

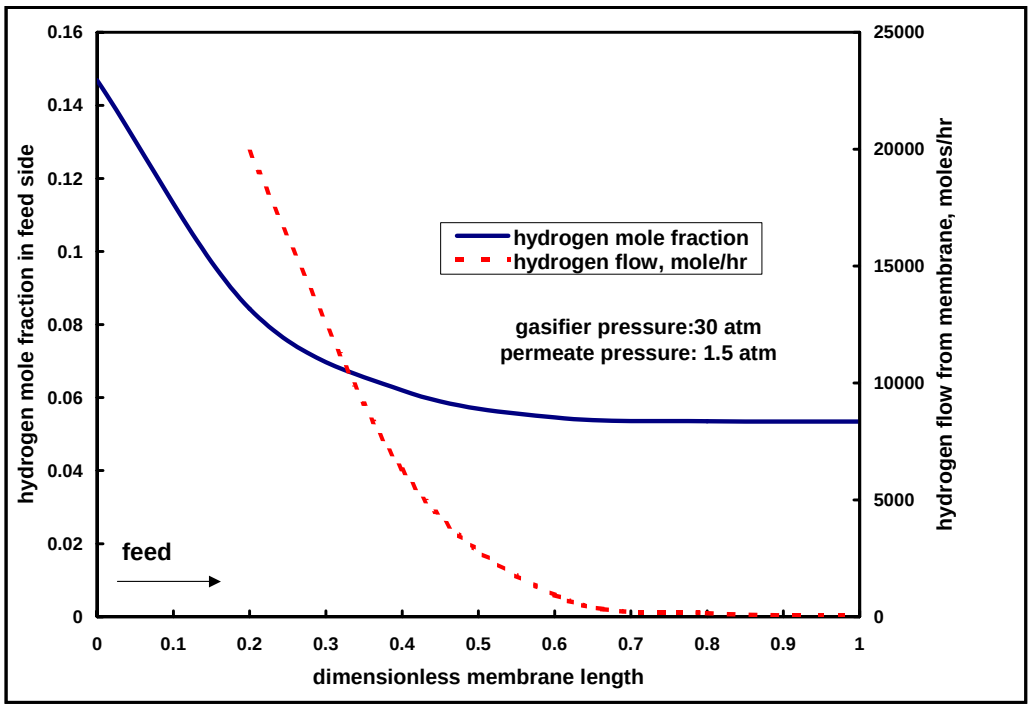


**Figure 5. Hydrogen concentration and hydrogen flux at different positions of the membrane as predicted by the model**

The two major assumptions of this preliminary simulation are the approach to equilibrium for both shift and reforming reactions in the gasifier and the proton conductivity of the membrane or the hydrogen permeability. These parameters will be evaluated in more detail based on literature data/information.

## OTHER ACTIVITIES

An industrial advisor meeting was held on March 2 at GTI. Representatives from ICCI (Illinois Clean Coal Institute), AEP (American Electric Power), Wah Chang (a Palladium membrane manufacturer), Schott Glass and ProTek Inc. (a high temperature membrane manufacturer representative) attended this meeting to discuss and review the project status.

A project kick-off meeting was held with the DOE program manager at DOE/NETL on March 4th.

## CONCLUSION

The construction of the high pressure/high temperature permeation unit was completed. The unit will allow screening and testing of membrane materials at the coal gasification temperature and pressure conditions up to 1100$^{o}$C and 60 atm respectively. The hydrogen flux that will be obtained from this unit will provide a meaningful and realistic basis for the membrane gasifier design and economic analysis. This is a first step that is critically important for the successful development of the membrane gasifier technology. Modeling efforts in this quarter also show the importance of maintaining a sufficient hydrogen partial pressure difference across the membrane to achieve a good membrane performance.

## PLAN FOR NEXT QUARTER

Hydrogen permeation testing will be conducted on the new permeation unit under typical gasification temperature and pressure conditions. Initial candidate membrane materials include simple Sr and Ba cerate-based perovskite ceramic materials. Dual phase cermet materials incorporating Pd, or Ni in the perovskite structure will also be tested. A complete membrane reactor model for a fluidized bed gasification system will be developed. The model will help guide the material development/screening, and provide the basis for the conceptual design of the membrane gasifier.

## REFERENCES

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2. T. Norby and Y. Larring, Solid State Ionics, P139, 137-137 (2000)