ABSTRACT

The objective of this project is to develop proton-conducting ceramic membranes for high temperature H₂ separation in coal gasification processes. GTI has developed a concept that incorporates a hydrogen-selective membrane within a gasifier for direct extraction of hydrogen from the coal-derived synthesis gas. This project addresses the membrane material development area of the overall membrane gasifier program. GTI has identified the ceramic material of the perovskite type as one of the best candidate materials for the H₂ separation application in the coal gasification processes. The preparation of the ceramic powders, perovskite membrane fabrication, hydrogen permeation testing and initial process evaluation were investigated in this project.

BCN (BaCe₀.₉Nd₀.₁O₃₋ₓ) and BCY (BaCe₀.₈Y₀.₂O₃₋ₓ) were selected for this study because of their high proton conductivities. Thick unsupported membranes (~0.05 cm) were prepared by uniaxial pressing or tape casting methods, followed by sintering at 1450 to 1550°C for 2~3 hours. Thin supported membranes (100~200 micron) were prepared by tape casting and lamination techniques. Metal components such as Ni, or Pd were also added to the membrane layer to increase the electronic conductivity and hydrogen flux.

A double-seal technique employing the sealant tapes made of glass and ceramic powders was developed and tested successfully to achieve a leak-tight seal for the tested membranes. The hydrogen fluxes for several unsupported BCN and BCY membranes were measured. At 900°C with 1 atm of pure hydrogen feed, the hydrogen flux ranged from 0.04 to 0.14 cc/min-cm², depending on the thickness. Limited flux data for the supported thin membranes and the membranes containing Pd or Ni were also obtained.

Preliminary process simulation based on the measured hydrogen flux shows that the hydrogen production efficiency using the novel membrane gasification reactor concept can be increased by more than 40% versus the conventional gasification process. Future work will need to continue improving the permeability and address the chemical and mechanical stability of the membrane materials.
EXECUTIVE SUMMARY

The objective of this project is to develop proton-conducting ceramic membranes for high temperature H₂ separation in coal gasification processes. GTI has developed a concept that incorporates a hydrogen-selective membrane within a gasifier for direct extraction of hydrogen from the coal-derived synthesis gas. The proposed membrane gasifier concept can potentially achieve thermal efficiency of 80% or higher and reduce the hydrogen product cost by more than 40% over the conventional gasification technologies. In addition to process simplification, this new concept can also reduce the cost of CO₂ capture for the coal gasification processes. This project addresses the membrane material development area of the overall membrane gasifier development program.

The ceramic material of the perovskite type has been identified as one of the best candidate materials for the H₂ separation application in the coal gasification processes. This type of material possesses a unique property of mixed protonic and electronic conductivity. Under a pressure gradient of hydrogen across the membrane, only hydrogen can permeate through it, resulting in a pure and clean hydrogen product. Its flux can be further increased by reducing its thickness and operating at high temperatures and pressures as in the coal gasification processes. This material was selected for further investigation in this project. The scope of work consists of four main tasks: ceramic powder preparation, membrane fabrication, membrane permeation testing and membrane process development.

Task 1. Ceramic powder preparation

The objective of the Task 1 is to prepare the powders needed to fabricate proton-conducting membranes. BCN (BaCe₀.₉Nd₀.₁O₃₋ₓ) and BCY (BaCe₀.₈Y₀.₂O₃₋ₓ) were the materials selected because they were shown in the literature to have the highest proton conductivity among the perovskite materials. Praxair was contracted to prepare 1 kg each of the powders. The powders possess the required high surface areas (5-10 m²/g), purity, phase composition and the specified dopant level.

Task 2. Membrane fabrication

Membrane disks in this project generally were made by two techniques: uniaxial pressing and tape casting. In the uniaxial pressing method, the perovskite powders were pressed in a die to form a membrane disk. The tape casting method involved the dispersion of the ceramic powders in a liquid medium that consisted of organic additives needed to obtain a plastic tape. The green disks or tapes were then sintered at 1450 to 1550°C for 2-3 hrs to densify the membranes.

Because thin membranes do not have adequate strength, they need to be supported on thicker porous support layers. The porous support was also fabricated from the same material as the dense layer to maintain the same thermal properties such as thermal expansion coefficient. Both the dense and the porous tapes were then laminated together.
and sintered. To sinter without delamination, the shrinkage rates of the dense layer and the support layer must match each other. This was achieved by adjusting the solid loading in each layer. Tape lamination was initially performed by roll calendering. Due to excessive stretching of tapes, warpage was observed as a common defect of the sintered samples. Flatter samples were obtained when the roll compaction force was reduced or by simply applying the uniaxial pressing method for the lamination process.

The successful preparations of the thick unsupported membranes (~0.05 cm) and the thin supported membranes (100–200 microns) have been repeatedly demonstrated in this project.

Metal components such as Ni, or Pd were also added to the membrane layer to increase the electronic conductivity and the hydrogen flux. Pd is a well-known material for use as a hydrogen membrane. NiO was used as a pore former to create porosity after NiO was reduced to Ni. Therefore, NiO addition to BCN and BCY yields a strong material that is ideal for the porous support layer. Several perovskite membranes containing Pd or Ni were also successfully fabricated in this project.

**Task 3. Membrane permeation testing**

Under this task, laboratory size membranes were tested in permeation test fixtures for the H₂ separation performances. Two test fixtures with different sealing techniques have been designed and constructed. The schematics of both test fixtures are shown below. The tube-in-tube configuration used a high temperature glass-based sealant to bond the membrane sample and the holder. The tube-against-tube configuration applied external mechanical load to achieve the tight seal. Both fixtures were successfully tested. However, the latter required good tube-to-tube alignment and a mechanically strong sample. For operation simplicity, the tube-in-tube configuration was chosen as the preferred membrane permeation testing method.

![Diagram of membrane permeation testing fixtures](image_url)

An improved sealing technique with the tube-in-tube configuration oriented vertically was also developed in this project. The membrane was positioned at the end of a holding tube with a small section of the inner wall cut off to provide a groove for holding the membrane. The membrane was sealed to the tube using two sealant tapes in a shape of O-ring, one above and the other below the membrane. The sealant was a mixture of glass and ceramic powders. Adequate seal was repeatedly achieved.
At least five sets of permeation data from the tests with acceptably low or undetectable leakage were obtained. They were all measured at 950°C and 1 atm with a 20 cpm H₂ feed gas on one side of the membrane and 6.5 cpm N₂ sweep gas on the permeate side. The disk samples had a diameter of 0.7 inch with thickness ranging from 140 µ to 600 µ. The samples varied from self-supporting (membranes thick enough to handle without a support layer) BCN, BCY and SCE (Eu-doped SrCeO₃ perovskite membrane) to supported BCN membranes. The H₂ flux varied from 0.036 cc/min-cm² for a 600µ self-supporting BCN to 0.137 cc/min-cm² for a 140µ BCN supported on a 290µ porous BCN. The data suggest that the thickness is one important parameter that can significantly affect the H₂ permeability of the perovskite membranes.

**Task 4. Membrane process development**

A conceptual membrane gasifier based on a fluidized bed gasifier and a tubular membrane module was developed. It appeared that the addition of the membrane module would not increase the gasifier dimensions significantly. A membrane gasification reactor model was developed to consider the H₂ permeability of the membrane, the kinetics and the equilibriums of the gas phase reactions in the gasifier, the operating conditions and the configurations of the membrane reactor. The results confirm that the hydrogen production efficiency using the membrane gasifier process can be increased by more than 40% over the conventional gasification technology.

Future work will need to continue improving the permeability and address the chemical and mechanical stability of the membrane materials. An initial study on the chemical stability issues for the perovskite membranes under the coal-derived syngas has been conducted. Other areas that need further development effort include scaling up the membrane size, reducing the membrane thickness, conducting conceptual design of the membrane gasifier reactor, performing bench scale testing for a small membrane module.
OBJECTIVES

The overall objective of the project is to develop the high temperature H₂ separation membranes that can be used within or near a gasifier for high efficiency, clean and low cost production of hydrogen at elevated pressures from coal. The project focuses on the membrane material development as a part of the overall effort in developing the novel membrane reactor technology for direct extraction of hydrogen from a coal gasifier. For the current year, the specific objective of the project is to develop fabrication and testing techniques for proton-conducting perovskite membranes for H₂ separation in the coal gasification application.

The project includes the following four tasks:

Task 1. Identify the candidate materials and prepare the powders

The objective of this task is to identify the promising proton-conducting perovskite membrane materials and prepare their powders.

Task 2. Membrane fabrication

This task is to develop fabrication techniques for making thin and dense ceramic membranes from the powders secured in the Task 1.

Task 3. Membrane testing

The objective of this task is to test the hydrogen flux for the membrane disks fabricated in the Task 2 in a laboratory permeation unit.

Task 4. Process development based on testing data

Based on the measured membrane performance from the Task 3, the feasibility of using the candidate membranes for the coal gasification application will be evaluated through modeling and process simulation.

INTRODUCTION AND BACKGROUND

As the US has begun the transformation process from a reliance on petroleum to the use of clean-burning hydrogen, hydrogen is expected to be the major energy carrier in the future hydrogen economy. With abundant coal reserve in the US, especially in Illinois, coal to hydrogen will play a crucial role as a source of hydrogen supply. However, the cost of hydrogen produced from coal gasification is currently not competitive to hydrogen from natural gas. There is urgent need to develop a breakthrough technology to lower the cost of hydrogen from coal.
GTI has developed a novel concept of a membrane reactor by incorporating a hydrogen-selective membrane near or within a gasifier for direct extraction of hydrogen from the coal synthesis gases. As more than 50~60% of the final hydrogen product is generated in the gasification stage, there is great potential of maximizing hydrogen production by separating hydrogen directly from the gasifier.

GTI has developed a multi-year road map for carrying out this concept to commercial success. The plan calls for development efforts on four major areas, membrane material development, membrane module development, membrane process development, and membrane gasifier scale-up. This project focuses on membrane material development and some initial efforts on membrane module development and process development.

The ceramic material of the perovskite type has been identified as the best candidate material for the H₂ separation application in coal gasification processes. This type of material possesses a unique property of mixed protonic and electronic conductivity. Under a pressure gradient of hydrogen across the membrane, only hydrogen can permeate through it, resulting in a pure and clean hydrogen product. The perovskite membranes may not be suitable for low temperature (<500°C) membrane shift reactor applications. The best working temperature range, 700~1200°C of this type of material will be ideal for the membrane gasification reactor applications.

The transport mechanism for H₂ separation using mixed conducting ceramic membranes can be described with the aid of Figure 1.

![Figure 1. H₂ gas separation through a ceramic membrane](image)

On the feed side, H₂ from the feed gas is oxidized to form protons and electrons:

\[
2H_2 \rightarrow 2H^+ + 2e^- \tag{1}
\]

Both protons and electrons are transported through the membrane to the permeate side where protons and electrons recombine to form H₂.
\[ 2H^+ + 2e^- \rightarrow 2H_2 \]  \hspace{1cm} (2)

Thus, the requirements for the ceramic membrane are:

- Protonic conductivity
- Electronic conductivity
- Dense ceramic
- Thin (5-15 µ) for reduced resistance

Additionally, the membrane must be fabricable into practical sizes using a simple and mass scaleable process.

![Figure 2. Conductivity of some perovskites [1]]

Iwahara et al. [1] identified doped perovskite materials based on BaCeO₃ and SrCeO₃ as mixed protonic and electronic conductors. The measured conductivities of some of these materials are presented in Figure 2. Rare earth elements such as Nd, Y, Yb, Eu, and Sc are partially substituted for Ce to enhance conductivity. These perovskites show high proton conduction under low O₂ partial pressures (for example in H₂ or H₂O atmospheres) and high electron conduction at high O₂ partial pressures (for example in O₂ containing atmospheres). When one side of the ceramic membrane is under H₂ and the other side is under a more oxidizing atmosphere, the membrane has a mixed protonic and electronic conduction. Nevertheless, the detailed mechanism of H₂ transport through a perovskite ceramic membrane can be complex. Furthermore, while most of the study focused on the proton conductivity of the perovskites, very few research groups have actually reported the hydrogen permeation data.[2-6] The project further explored the
potential of this group of materials for the application of the membrane gasification reactor to produce hydrogen from coal.

EXPERIMENTAL PROCEDURES

Task 1. Identify the candidate materials and prepare the powders

BCN (BaCe$_{0.9}$Nd$_{0.1}$O$_{3-x}$) and BCY (BaCe$_{0.8}$Y$_{0.2}$O$_{3-x}$) were the materials selected because they have the highest proton conductivity among the perovskite materials according to Iwahara’s data [1]. Neodymium (Nd) and Yttrium (Y) are two common dopants for the BaCeO$_3$ compound. Praxair Surface Technology was therefore contacted to provide 1 kg each of the powders. This is more cost effective than preparing the powders at GTI. The powders possess the required high surface areas, purity, phase composition and the specified dopant level. The obtained powder properties were:

- **BaCe$_{0.9}$Nd$_{0.1}$O$_{3-\delta}$ (BCN)**
  - Surface area = 4.3 m$^2$/g
  - Mean particle size = 0.7 $\mu$m
  - Bulk density = 1.33 g/cc
  - X-ray diffraction - phase pure BaCeO$_3$
  - Chemical purity - 99.9%

- **BaCe$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BCY)**
  - Surface area = 4.0 m$^2$/g
  - Mean particle size = 0.5 $\mu$m
  - Bulk density = 1.38 g/cc
  - X-ray diffraction - phase pure BaCeO$_3$
  - Chemical purity - 99.9%

Task 2. Membrane fabrication

Membrane disks in this project generally were made by two techniques: uniaxial pressing and tape casting.

In the uniaxial pressing or isostatic pressing method, the perovskite powders were pressed in a die at 15,000 psi (1000 atm) to form a membrane disk with a diameter of 1 to
3 cm and a thickness of 0.045 to 0.07 cm. The green disk was then sintered at 1450 to 1550°C for 2-3 hrs to densify the membranes.

The tape casting method involved the dispersion of the ceramic powders in a liquid medium that consisted of solvent, binder, plasticizer and other additives needed to obtain a plastic tape with proper powder packing, drying and release properties. For the tapes prepared under this project, GTI’s proprietary tape casting solvent composition was used. To minimize the use of the costly powders, techniques were developed to prepare smaller than normal slurry volume to learn the fabrication behavior of the materials. Powder loading in a tape is a parameter that affects the sintering property. It is usually less than 50 volume percent and normally 35 to 45 %. A tape with high powder loading can be sintered at a relatively lower temperature with less shrinkage. Similar to the pressed disks, the green tapes were sintered at 1450 to 1550°C for 2-3 hrs to densify the membranes.

Membranes with Porous Support

If the membrane is thin as is often desired, the dense membrane needs to be layered with a thicker porous support for strength. The porous support was also fabricated from the same material as the dense layer to maintain the same thermal properties such as thermal expansion coefficient. Three routes of fabricating the membranes with porous supports were investigated:

1. Pellet fabrication by powder pressing and layering with porous supports.
   A layer of BCY powder was sandwiched between two layers of BCY powders containing about 10 volume percent of a pore former. After pressing and sintering, the two outer layers would form the porous supports. The middle layer could have a thickness of 200 to 300 microns, which is the minimum thickness that this method could produce.

2. Layering of cast tapes by roll calendering or uniaxial pressing.
   The process was based on the tape casting and the laminating processes for flexibility in thickness design, scalability, and cost effectiveness. The process for fabricating a supported membrane from separate BCN and porous BCN (PBCN) tapes is schematically described in Figure 3. The tapes were laminated by such techniques as roll calendering, or uniaxial pressing. During the lamination process, any void in the green tape was squeezed out. In the case of roll calendering, the individual layer may even be thinned down to the desired level. For example, a 3-mil (1 mil = 25 µ) BCN tape and three layers of BCN with pore formers totaling 40mils were roll laminated to a thickness of 20 mils. The rolled laminate therefore consisted of a 1.5-mil BCN layer and a 18.75-mil porous layer. During sintering, the thickness was further reduced by 24%, making the BCN layer 1.14 mils and the porous support, 14.63 mils or 370 µ.
For the porous supported membranes, the sintering rate for the membrane and the support layers have to be matched. Since it is desired to maximize the porosity of the porous layer, the shrinkage rate of the membrane often has to be adjusted to match that of the porous layer. This is often done by adjusting the powder loading of the membrane tapes. For the BCN, the tapes with powder loading of 37-44 volume percent were prepared and sintered. The dry BCN tapes as thin as 2 mils (50 µ) could be obtained. After pressing, the BCN tape with 44% loading sintered well between 1500 and 1550°C with 24% linear shrinkage.

The tapes for the porous BCN support layers were also formulated with the same binder system. They initially contained 7 volume percent graphite powder pore former. The solid loading for these tapes were 37-45 volume percent solids. Pressed tapes sintered to 89% dense with 22% linear shrinkage. The pore former in the porous support was later increased to 25 volume percent, which sintered to about 65% dense. Sintering shrinkage with this more porous support was about 28% but remained compatible with the shrinkage of the dense membrane layer.

3. Sandwiching a thin membrane tape between two layers of powder with pore former
This method is a combination of the above two methods, where the middle dense layer was made by the tape casting and placed between two layers of powders with pore formers. The powder/tape/powder layered membrane was then pressed under 15,000 lb load and sintered at 1500°C for 2 hrs. The resulting pellets were flat but did not produce satisfactory quality with cracks formed on the surface.

The successful preparations of the thick unsupported membranes (~0.05 cm) by either the tape casting or the pressing and the thin supported membranes (100~200 microns) by the above method 2 have been repeatedly demonstrated in this project.

Metal Addition to BCN and BCY

Metals are added to the proton conducting ceramics to increase the electronic conductivity and improve the overall H₂ transport. To study the effect of metal addition on sintering characteristics, disks of BCN and BCY with and without metals were pressed and sintered. The metals were NiO (from Novamet, 25 weight percent) and Pd
(0.5µ from Alfa Aesar, 7% by weight) powders. They were added simply by dry mixing with the perovskite powders. After pressing, the disks were sintered at 1500°C for 2 hrs.

The tape casting method was also used to fabricate the membranes containing the metals. The thin tapes of BCN containing 5 volume percent of Pd were prepared and roll laminated with thick tapes of BCN containing 10 volume percent of graphite pore former. Similarly, thin tapes of BCY containing 7 volume percent Pd were prepared and roll laminated with thick tapes of BCY containing 10 volume percent graphite pore former. These laminates were sintered between 1400 and 1500°C for 2 hrs.

BCN or BCY containing NiO cannot be an effective H₂ separation membrane because NiO reduces to Ni and leaves voids in the membrane. Instead of the organic pore formers used for the porous supports, NiO was used as a pore former to create porosity after NiO was reduced to Ni. Therefore, NiO addition to BCN and BCY yields a strong material that is ideal for the porous support layer. The reduction process of NiO is a good means of controlling the support layer porosity and the Ni product may act as a catalyst to the relevant reactions on the membrane surface.

**Task 3. Membrane testing**

**Permeation Testing Apparatus**

Initially, the membrane samples were tested in a permeation unit with a tube-in-tube configuration positioned horizontally as shown in Figure 4. The feed gas entered the unit from the right hand side of the diagram and encountered the membrane disk that was attached to the tip of a membrane holding tube before exiting the unit. A sweeping gas, generally nitrogen, entered the unit from the left hand side of the diagram through a tube within the membrane holding tube. The sweeping nitrogen gas along with the permeate hydrogen was analyzed by gas chromatography (GC) to determine the H₂ flux. In this work, the flow rate of the feed gas was in the order of 20 STP cc per minute (cpm) and that of the sweeping gas was about 6 cpm.

![Figure 4. Tube-in-tube membrane test fixture design](image)

1= feed inlet, 2=feed outlet, 3=sweep inlet, 4=sweep + permeate
The horizontal tube set-up, however, was later turned vertical for gravity support of the membrane. Figure 5 shows the picture of the current permeation unit. The unit was designed to operate at ambient pressure and temperatures to 950°C.

Figure 5 The hydrogen permeation unit with tube-in-tube configuration

Membrane Seal Development

To attach the membrane disk to the end of the membrane holding tube is not a trivial task. The circular membrane needs to be sealed against the tube along the edge to achieve no or minimum “crossover” or leakage between the feed gas and the sweeping gas. Leak test was always conducted for each membrane sample using He as the feed gas before the hydrogen permeation testing. The detection of He in the sweeping or the permeate side indicated leakage. The measurement of the flow rates for both inlet and outlet of the sweeping gas could also be used to detect any high leakage rate. However the leakage could be from the gaps of the seal or the pinholes of the membrane. To eliminate the leakage problem caused by the membrane itself, dense alumina or zirconia materials, which can be fabricated into gas impermeable disks relatively easily were used as the test samples during the initial stage of the seal development.

Due to the high temperature operation, the initial sealing materials tested included high temperature cements such as Aremco 516, Cotronics HP alumina. In some cases, the cement were mixed with the ceramic powders or glass powders as the sealing material. However, the cement-based sealants did not produce satisfactory results.
A tube-against-tube test fixture was assembled and evaluated as an alternative permeation testing approach. The design is shown in Figure 6. In this design, two tubes of similar size were aligned against each other and the membrane sample was sandwiched between the tubes. Between the sample and the two opposing tubes were two high temperature compressive seal materials, similar to the conventional O-ring seal. Alignment for this set-up was very critical. Guide pins were used to align the tubes. The tubes were pushed against each other as the guide pins were locked in place to maintain a compression load on the sample. Although some success was achieved for the tube-against-tube configuration for a palladium membrane test, this set-up was later abandoned because of the difficulty of the alignment and the concern of the membrane strength. The membrane was prone to cracking under the load with this set-up.

![Figure 6. Tube-against-tube set-up](image)

At the suggestion of Professor J. Lin of the University of Cincinnati, the development of using glass sealant was initiated. The first composition was a mixture of 80 volume percent of glass with a size −100 mesh and 20 volume percent of the ceramic powders with a submicron size. The glass provided the bonding strength while the ceramic powder kept the thermal expansion coefficient of the sealant material matching that of the membrane. They were mixed and cast to form a sealant tape. The tape was cut out in a shape of O-ring to bond the sample to the membrane holding tube in the tube-in-tube set up in Figure 5. Since the slurry used for the tape casting was essentially a paste, it was also used to touch up the seal around the edge of the sample to repair any unfilled gap or opening. After assembly in the test fixture, the sample was heated to 950°C overnight and held at this temperature for 1 hr before cooling the sample down to the test temperature of 900°C or below.

Another improvement in the sealing technique was made by fabricating a funnel-shaped metallic permeation tube. The metal is of 400 series stainless steel, which has a thermal expansion coefficient closely matching that of the ceramic membrane. The difference between the original permeation unit and the new fixture is described with the aid of Figure 7. In the old fixture, the membrane holding tube was a 0.75-in dense alumina
tube, onto which the membrane was sealed against. With the new fixture, the disk sample was positioned at the end of a holding tube with a small section of the inner wall cut off to provide additional seal to the membrane. The membrane was sealed to the tube using two glass tapes, one above and the other below the membrane. The entire membrane tube assembly was then installed in the permeation unit, first fired to 450°C in air to burn out any organic compound in the glass tapes, followed by flowing with N₂ to 950°C to melt or soften the sealant. At 950°C with this set-up, no gas leakage was detected for several membrane tests. Subsequent permeation tests, therefore, were all conducted at 950°C using this sealing technique.

Figure 7. Comparison of the old and new sample holder

Task 4. Process development based on testing data

Modeling of Membrane Gasification Reactor

To evaluate the feasibility and the potential benefits of using the perovskite membranes for direct extraction of hydrogen from the coal gasifier, simulation was performed for a membrane reactor located within a fluidized bed gasifier. The free board area or the disengagement zone of a fluidized bed gasifier provides a convenient location for the membrane reactor. In this Task, a tubular membrane reactor configuration is used in the simulation. Figure 8 shows a schematic for one of the membrane tubes within a fluidized bed gasifier. The coal syngas generated in the gasification zone at the lower section of the fluidized bed enters the membrane reactor module. The membrane tube is assumed to be
made of the mixed proton/electron conducting perovskite material. Hydrogen is removed from the tube side of the membrane and the non-permeate syngas exits the gasifier from the shell side. In this preliminary study, contaminants generated from coal gasification are not considered. In reality, a stable, durable and robust membrane material and the reactor module will need to be developed.

Figure 8. Schematic diagram for a tubular membrane within a fluidized bed gasifier

The major assumptions of the model are isothermal operation, no pressure drop along the length of the membrane tubes, and plug-flow behavior. Only carbon, hydrogen and oxygen are considered in the mass balance.

A mass balance for the feed side of the membrane tube yields

$$\frac{\partial F_i}{\partial x} - R_i + J_i = 0$$

(3)

where $F_i$ is the molar flow rate of component $i$, $x$ is the length of the membrane tube, $R_i$ is the reaction rate for forming component $i$, and $J_i$ is the permeation rate of component $i$.

Chemical kinetics is employed to describe the rates of uncatalyzed reactions in the feed side of the membrane. This approach was used by Karim and Metwally[7] satisfactorily for modeling of the reforming of natural gas. A reaction scheme comprising 14 chemical species and 32 elemental reaction steps has been employed. The chemical species considered are six major gas components in the gasifier: CH$_4$, O$_2$, CO, H$_2$, CO$_2$, and H$_2$O, and eight radicals: OH, CH$_3$, H, O, HO$_2$, H$_2$O$_2$, CH$_2$O, and CHO. The reaction rate for each species $R_i$ can be described as
\[ R_i = \sum_{j=1}^{64} \alpha_{ij} K_j \prod_{l=1}^{n} (C_l)^{\alpha_{lj}} \] (4)

where \( \alpha_{ij} \) is the stoichiometric coefficient of the \( i \)-th species appearing in the \( j \)-th reaction with a positive sign for the product and a negative sign for the reactant, \( K_j \) is the rate constant for the \( j \)-th reaction, \( C_l \) is the molar concentration of the species \( l \), and \( \prod_{l=1}^{n} (C_l)^{\alpha_{lj}} \) denotes multiplication of \( (C_l)^{\alpha_{lj}} \) for species \( l \) appearing in the reactants of the \( j \)-th reaction. The detailed reaction steps and the rate constants can be found from reference [7]. Because both forward and backward reactions are considered, there are effectively 64 reaction steps altogether.

If the candidate membranes contain metal such as Ni, catalytic reactions can take place. To consider the catalytic reactions, additional 14 reaction steps for the reaction mechanism of CH\(_4\) oxidation on Pt [8] are added to the original 32 reaction steps. Furthermore, the reaction steps involving catalysts have replaced the same reaction steps without catalyst. For example, the following reaction step

\[ \text{CH}_4 = \text{CH}_3 + \text{H} \quad \text{Rate (forward)} = 1.0 \times 10^{13} \exp(85,000/RT) \] (5)

is replaced by

\[ \text{CH}_4 + \text{M} = \text{CH}_3 + \text{H} + \text{M} \quad \text{Rate (forward)} = 1.0 \times 10^{17} \exp(86,000/RT) \] (6)

**Hydrogen Permeation in Mixed Proton-Electron Conducting Perovskite**

In the mixed proton-electron conducting perovskite, the driving forces for hydrogen transport are chemical and electrical potential gradient. Without the use of electrical circuit, the flux of protons is compensated by a simultaneous flux of electrons or electron holes to maintain electrical neutrality. In a simplified form, the hydrogen flux can be expressed in the form of the Wagner equation [9,10]:

\[ J_{H_2} = -\frac{RT}{4F^2L} \left( \frac{\sigma_{H^+}}{\sigma_{H^+} + \sigma_e} \right) \left( \ln(p_{H_2}^f) - \ln(p_{H_2}^p) \right) \] (7)

where \( R \) is the gas constant, \( F \) is the Faraday constant, \( L \) is the membrane thickness, \( \sigma_{H^+} \) is the proton conductivity, \( \sigma_e \) is the electronic conductivity, \( p_{H_2}^f \) is the partial pressure of hydrogen in the feed side of the membrane and \( p_{H_2}^p \) is the partial pressure of
hydrogen in the permeate side. The conductivity term, \( \frac{\sigma_{\text{H}_2}}{\sigma_{\text{H}_2} + \sigma_{\text{el}}} \), is determined from the hydrogen flux measured in the Task 3.

Because the perovskite membrane offers 100% selectivity for hydrogen, \( J_i \) is zero for all the species except hydrogen. Equation (3), in combination with Eqs. (4) and (7) can be solved for all 14 species with the known boundary conditions at the inlet of the membrane tubes. These boundary conditions are determined by the flow rates and the compositions of the coal syngas from the gasification zone below the membrane module. A GTI gasification model U-GAS® was used to estimate the gas flow rates and the compositions from a fluidized bed gasifier.

RESULTS AND DISCUSSION

Task 1. Identify the candidate materials and prepare the powders

One kilogram each of BCN and BCY powders with the required high surface areas, purity, phase composition and the specified dopant level were purchased from Praxair as described earlier.

Task 2. Membrane fabrication

**Sintering Temperature**

To determine the sintering behavior of the new powders, disks were pressed from the powders and sintered at recommended temperatures. Two disks with a diameter of 1.125 inch and a thickness of 0.025 inch were therefore pressed at 15,000 psi from the BCN powders. Upon sintering at 1500°C for 2 hrs, one disk was flat and crack-free but the other disk had edge cracks. The good disk had a density of 6.35 g/cc and was considered dense. 1500°C was therefore used as the initial baseline sintering temperature for BCN.

**Unsupported Membranes**

Unsupported or self-supported membranes were generally much thicker than the supported ones. The thinnest unsupported membranes that were made in this project are about 500 microns from the uniaxial pressing method and about 300 micron from the tape casting method. The unsupported membranes for both BCN and BCY can be routinely made without difficulty. Successful permeation tests for these membranes were also achieved. However, one of the main objectives of this project is to fabricate thin and supported membranes. The results of the development effort in fabricating the supported membranes are discussed below.

**Supported BCN Membranes**
The initial samples of the supported BCN membranes made by the tape casting followed by lamination using roll calendering were small, 0.5 inch in diameter in the green state. The sample shrank to under 0.4 inch in diameter after sintering. A micrograph of such a sintered laminate is shown in Figure 9. Note that the active membrane layer, which is responsible for the proton transport appears dense. But the support layer appears to contain poorly connected pores. The porosity of this porous support layer was only 11%, which probably could not provide adequate passage for the gas flow. The hydrogen flux could be restricted by the support layer.

![SEM Photo of a BCN Bilayer Membrane](image)

Figure 9. SEM micrograph of a sintered BCN membrane supported by a porous BCN layer

When the size of the supported BCN was increased to about 1 inch, cracking became a problem during sintering. The membrane cracking problems actually occurred for both types of membranes made from the tape casting as well as the powder pressing. For the membranes made by the pressing, sintering results were improved by adding a small amount of binder solution to the powder as a pressing aid. Similar improvements were observed with thicker disks. These observations indicated that poor green strength was the cause of the poor sintering results. Green strength, however, could not be a reason for the cracking problem with the BCN tapes because they already contained enough binder for the tape casting process. The cracking problem for the cast membranes were solved by changing the lamination procedure. The initial laminates were made by the roll calendering. After changing to the uniaxial pressing for the green tapes, the pressed laminates sintered much better. The uniaxial pressing became the standard lamination process. As large as 1.0 inch diameter disks have been routinely obtained.
Therefore, the established fabrication process for the supported membrane is:

- Tape cast thin membrane layer.
- Tape cast porous support layer.
- Cut tapes to size and laminate by uniaxial pressing.
- Sinter at 1500 – 1550°C for 2-3 hrs.
- Measure size and inspect for obvious defects.

**Supported BCY Membranes**

Given that the BCY powder had very similar characteristics as the BCN, it was assumed that BCY sintered similarly as the BCN. Powder sintering studies by pressing disks from the powder was therefore omitted for the BCY.

For the tape casting method, the same binder system was also applied to the BCY. The first BCY tape contained very high powder loading (54 volume percent), and hence, sintered with less shrinkage, 19-20%. The first porous BCY support tape contained 10 volume percent graphite pore former and had 45 volume percent solid loading. The tapes of BCY with and without the pore former were roll laminated and sintered at 1550°C for 2 hrs to make the BCY membrane with the porous support. The sample was flat and had no visible defects. The results were also repeatable. A micrograph of the sintered laminate with the dense membrane layer of about 10µ in thickness is shown in Figure 10. Like the BCN support layer, the BCY support layer does not seem to contain sufficient porosity as required for efficient gas supply and removal to and from the membrane surface. Also, the solid loading of 54% for the BCY layer appeared high and the tape was brittle for the roll lamination.

The solid loading of the BCY tapes were, therefore, reduced to 38-46 volume percent and the tapes became flexible and easy to handle. These tapes were roll laminated together with the porous BCY tapes. Because the overall thickness of the membrane was reduced by the laminate process, the disk warped during sintering, presumably due to the excessive rolling action. When the rolling speed was reduced to just bond the layers together, flat and crack free samples were obtained. Alternatively, good quality of tapes could be obtained by, instead of rolling, simply pressing the tapes at a pressure as low as 3,000 psi. In these BCY fabrication studies, the tapes were not made thinner than 4 mils (100 µ) thick and sintered to no less than ~3mils (75µ). Sintering was performed at 1500 to 1550°C for 2-3 hrs. The established process for the BCY membrane, therefore, follows the same procedure described earlier for the BCN.
Metal Addition to BCN and BCY

To study the effect of metal addition on the sintering characteristics, the disks of the BCN and the BCY with and without the metals were pressed and sintered. The results after membrane sintering are summarized in Table 1.

**Table 1. Comparison of membrane disks with and without metal addition**

<table>
<thead>
<tr>
<th>Membranes</th>
<th>No metal</th>
<th>NiO addition</th>
<th>Pd addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCN</td>
<td>good</td>
<td>good</td>
<td>warped</td>
</tr>
<tr>
<td>BCY</td>
<td>good</td>
<td>flat, stuck to sintering support</td>
<td>good</td>
</tr>
</tbody>
</table>

As mentioned earlier, the supported BCN or BCY could be sintered well with the established fabrication procedure. From Table xx, it appears that NiO addition only worked for the BCN, but not for the BCY. On the other hand, Pd addition only worked for the BCY, but not for the BCN. It is suspected that NiO may have formed a low melting phase with the BCY, which caused the membrane to stick to the sintering support plate. Good BCY membranes with NiO could only be prepared with a lower sintering temperature, 1475°C. The BCN laminates with Pd addition warped severely and cracked during sintering. However, the BCY laminates with Pd addition sintered well without visible defects if they were thicker than 50 microns.
Task 3. Membrane Testing

Palladium-Gold Membrane Testing

A commercial Palladium-Gold alloy (Pd/Au 80/20) membrane of 75 µ thickness was tested for their hydrogen flux in the tube-against-tube test fixture as shown in Figure 6. A feed gas with 80% of H₂ and 20% of He was fed to the upper tube at a rate of 25 cpm and a N₂ gas at 18 cpm was fed to the lower tube to sweep away the H₂ permeate. Test was conducted at different temperatures. Gas analysis of the permeate by GC showed only H₂ and N₂ in the gas stream without any He or O₂, indicating a tight seal. The measured fluxes at different temperatures are shown in Figure 11. The hydrogen flux in terms of the permeability are in the order of $2\sim3 \times 10^{-9}$ mole/s/m/Pa$^{1/2}$, which are comparable to the typical hydrogen flux of the palladium membranes reported in the literature [11].

![Permeation Data for Au-Pd Membrane](image)

**Figure 11.** Permeation data for Au-Pd film obtained with the tube-against-tube assembly

Unsupported Membranes

As described earlier, adequate seal was achieved with the improved sealing techniques in the test fixture shown in Figure 5. Several unsupported or self supported BCN or BCY membranes made by either the tape casting or the uniaxial pressing were successfully tested for their hydrogen flux. The testing results for each test are briefly described below:
• Test 04OC15 – The sample was a self-supported BCN made by pressing the powders into a disk and sintering the disk at 1550°C for 3 hrs. The thickness was 600 µ. The test was conducted at 950°C. With 20 cpm He as the feed gas, no He was detected in the permeate indicating a good seal. The feed gas was changed to H₂ over an hour period by increasing the H₂ content in steps. The slow change was to prevent sudden change in the membrane lattice structure by H₂ introduction that may potentially cause the membrane to crack. Under the H₂ feed, the measured H₂ in the permeate was to 0.024 cpm or 0.036 cpm per cm² of the membrane area.

• Test 04OC28 – The sample was a self-supported BCN made by the tape casting technique. The thickness was 533 µ. The tape was heated to 970°C and held at this temperature for 2 hrs. Test was conducted at 950°C. With a 20 cpm He feed and a 6.8 cpm N₂ sweep gas, no He was detected in the permeate. The feed gas was changed to a gas mixture of 50H₂/50He and a H₂ flux of 0.026 cpm was measured. The feed gas was then changed to 20 cpm pure H₂ and a H₂ flux of 0.042 cpm was measured. The feed gas was switched back to He again and no He was detected in the permeate side, confirming the integrity of the seal.

• Test 04NV5 - The sample was a self-supported 305 µ BCY disk made by the tape casting technique. The testing procedure was similar to that of Test 04OC28. No leakage was detected before and after the test. The measured H₂ fluxes were 0.03 and 0.09 cpm per cm² of the active area with 50H₂/50He and H₂ feeds, respectively. Two Eu-doped SrCeO₃ membrane disks originally fabricated from another project were also tested in the permeation unit shown in Figure 5.

• Test 04AG25 – The sample was a self-supported Eu-doped SrCeO₃ disk (SrCe₀.⁹Eu₀.₁O₃) made from the tape casting method. To increase the membrane strength, two tapes were laminated together to form a membrane with a thickness of 15 mils or 380 µ. Small He leakage rate of 0.119 cpm was detected before the test. When He was changed to H₂, permeation rate was measured at 0.194 cpm. Since the gas leakage was detected with He, this measured H₂ permeate was corrected by subtracting the equivalent H₂ leakage rate, which is 1.4 times of the He leakage rate, assuming the gas leakage follows the mechanism of the Knudsen diffusion. (The Knudsen diffusion rate is inverse proportional to the square root of the molecular weight.) The calculated net H₂ permeation through the membrane was 0.027 cpm or 0.023 cpm per cm² of the membrane area.

• Test 04OC22 - The sample was a self-supported SrCe₀.⁹Eu₀.₁O₃ made by the tape casting technique. The thickness was 584 µ. A He leak to the permeate of 0.008 cpm was measured. Based on the measured active area of the sample and by correcting for the minor leak observed at the end of test, the calculated H₂ flux was 0.04 cpm per cm² of the membrane area.
Table 2. Measured H2 flux for samples tested with the improved sealing technique in the funnel-shaped test fixture

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Sample</th>
<th>Thickness</th>
<th>Initial He Leak, cpm</th>
<th>Flux, 50% H2, cpm</th>
<th>Flux, pure H2, cpm</th>
<th>Final He Leak, cpm</th>
<th>Corrected H2 Flux, cpm/cm2</th>
</tr>
</thead>
<tbody>
<tr>
<td>04AG25</td>
<td>SrCe0.9Eu0.1O3</td>
<td>381</td>
<td>0.119</td>
<td>N.A.</td>
<td>0.194</td>
<td>N.A.</td>
<td>0.023</td>
</tr>
<tr>
<td>04OC15</td>
<td>BCN</td>
<td>600</td>
<td>0</td>
<td>N.A.</td>
<td>0.024</td>
<td>0</td>
<td>0.036</td>
</tr>
<tr>
<td>04OC22</td>
<td>SrCe0.9Eu0.1O3</td>
<td>584</td>
<td>0</td>
<td>N.A.</td>
<td>0.048</td>
<td>0.008</td>
<td>N. A. 0.040</td>
</tr>
<tr>
<td>04OC28</td>
<td>BCN</td>
<td>533</td>
<td>0</td>
<td>N.A.</td>
<td>0.026</td>
<td>0.042</td>
<td>0.027 0.059</td>
</tr>
<tr>
<td>04NV04</td>
<td>supported BCN</td>
<td>140</td>
<td>0</td>
<td>0.044</td>
<td>0.085</td>
<td>0.0015</td>
<td>0.048 0.137</td>
</tr>
<tr>
<td>04NV05</td>
<td>BCY</td>
<td>305</td>
<td>0</td>
<td>0.028</td>
<td>0.058</td>
<td>0</td>
<td>0.030 0.090</td>
</tr>
</tbody>
</table>

The measured H2 fluxes for the tests performed with the improved sealing technique in the funnel-shaped sample holder were obtained under the low leakage conditions. These data, which are more reliable are summarized in Table 2. The data appear to be a function of the thickness, as expected. Measured fluxes under 50H2/50He and pure H2 are plotted as a function of the membrane thickness in Figure 12. It is also interesting to note that the slope of the lines for 50H2/50He is much lower than that for H2. This means that as the membrane becomes thicker, the effect of H2 partial pressure in the feed stream becomes less important. H2 partial pressure in the feed side not only is the driving force for H2 transport, it also affects the conductivity of the membrane. Similarly, the H2 partial pressure in the permeate side also affects the H2 conductivity in a similar manner.

![Measured H2 Flux @ 900°C vs. Membrane Thickness](image_url)

**Figure 12.** Measured H2 flux at 950°C for various membranes
Supported Membranes

The supported membranes are difficult to make as mentioned earlier. Even though some flat and crack-free disks were obtained, very few permeation tests were successful. The hydrogen permeation flux for one supported BCN membrane and another supported BCY were measured, after correcting for the small leakage rate.

- Test 04NV4 - The sample was a 140 µ dense BCN supported on a 292 µ porous layer. Test was conducted at 950°C. With 20 cpm He feed and 6.8 cpm N₂ sweep gases, no He was detected in the permeate. A H₂ flux of 0.044 cpm was measured with a 50H₂/50He feed gas. And a H₂ flux of 0.085 cpm was measured with a pure H₂ feed gas. The feed gas was changed back to He at the end of the test and a He leak rate of 0.0015 cpm was detected. The measured H₂ fluxes after correcting for the small leak translated to 0.048 and 0.137 cpm per cm² active area with 50H₂/50He and H₂ feeds, respectively. Because of its low leakage rate, the data of this test is included in Table 1 and Figure 11.

- Test 04NV16 - The sample was a 90 µ dense BCY supported on a 343 µ porous BCY layer for a total thickness of 434 µ. He leak was 0.010 cpm in the beginning. In H₂, the measured flux was 0.062 cpm. At the end of test, He leak had increased to 0.027 cpm. The measured flux in H₂ after leak correction was 0.036 cpm.

Membranes with Metal Addition

Although the membranes with metal addition, Pd or NiO, have became available early on for the permeation tests, inadequate seal disqualified the results of the early tests. The following three tests, which showed reasonable hydrogen flux after correcting the He leakage, are discussed below:

- Test 04JN23 - This test used a trilayer sample consisting of a 32 µ BCY+6.5% Pd sandwiched between a 63µ and a 300 µ porous BCY layers. The total sample thickness was 395µ or 15.5 mils. During the test, the thinner BCY layer faced the permeate side. At 950°C, with a feed gas of 80H₂/20He at 30 cpm and a sweep gas of N₂ at 10 cpm, the measured H₂ flux was 0.032 cc/min- cm². It should also be pointed out that as discussed under the BCY Fabrication section, the BCY layer had only about 11% porosity. Because of this low porosity, the support layer may itself be acting as a solid membrane and decrease the effect of the Pd in the membrane layer.

- Test 04JN0629 - The sample was a trilayer sample consisting of a 200µ dense BCY layer sandwiched between two equally thick porous BCY+NiO layers. The total sample thickness was 109 µ. The purpose of the NiO was to provide strength to the trilayer, increase porosity in the support layer, and catalyze the reactions on the membrane surfaces. Both the feed and the permeate sides of the
membrane were first subjected to a 80H₂/20He gas at a flow rate of 16 cc/min for two hours. The NiO was reduced to Ni and porosity was created in the support layer. The leak test with He showed 0.7 cpm in the permeate side. The measured H₂ permeation rate was 1.2 cpm with a pure hydrogen feed. The hydrogen flux, after correcting for the He leakage rate was 0.176 cc/min-cm². Tests under the similar flow conditions were carried out at 850 and 750°C. However, the temperature variation seemed to have insignificant effect on the H₂ flux.

- Test 04JL08 – The sample was a trilayer membrane consisting of a 200µ dense BCN layer sandwiched between two equally thick porous BCN+NiO layers. The total sample thickness was 85 µ. This sample had similar assembly as the trilayer BCY used in Test 04JN29. The H₂ permeation rates after correcting for the He gas leakage were 0.29 cc/min-cm² when N₂ sweep rate was 4.8 cpm and 0.32 cc/min-cm² when the sweep rate was 13.2 cpm.

**Task 4. Process development based on testing data**

The conductivity term, \( \frac{(\sigma_{H^+})(\sigma_{el})}{\sigma_{H^+} + \sigma_{el}} \), in Eq. (6) needs to be determined before the simulation can be performed. The experimentally measured hydrogen flux for the BCN membrane containing Ni was first used to calculate the value of \( \frac{(\sigma_{H^+})(\sigma_{el})}{\sigma_{H^+} + \sigma_{el}} \) based on Equation (6). The obtained value was 0.004 S/cm, which is in the same order of magnitude as the conductivity reported in the literature [1]. However, the flux measured in this work was at ambient pressure. The commercial gasification process is expected to operate at high pressures, 30 atm and above. In an another project with ICCI (DEV03-1), GTI has conducted the measurement for the hydrogen flux at higher pressure and found that the conductivity term could be increased by about twice when the feed pressure was increased from 1 atm to 12 atm.[12] In this project, the value of \( \frac{(\sigma_{H^+})(\sigma_{el})}{\sigma_{H^+} + \sigma_{el}} \) was assumed to be a constant value of 0.01 S/cm.

The coal syngas flow rates and the compositions calculated from GTI's U-GAS® model are listed in Table 3 along with other operating conditions and parameters. The Illinois #6 coal was used for this example. The gasifier diameter in the freeboard region estimated from the U-GAS® model was 70 cm for a 200 tone per day (TPD) coal feed without the membrane module. The diameter was increased to 100 cm to accommodate the tubular membrane module. The membrane thickness was assumed to be 5 µ.
Table 3. Operating conditions and parameters used in the simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>coal feed, TPD</td>
<td>200</td>
</tr>
<tr>
<td>steam feed to gasifier, TPD</td>
<td>119</td>
</tr>
<tr>
<td>oxygen feed, TPD</td>
<td>120</td>
</tr>
<tr>
<td>steam feed to shift reactor, TPD</td>
<td>54</td>
</tr>
<tr>
<td>temperature, C</td>
<td>1100</td>
</tr>
<tr>
<td>coal syngas flow rates, Nm/hr</td>
<td>19425</td>
</tr>
<tr>
<td>pressure, atm</td>
<td>60</td>
</tr>
<tr>
<td>gasifier diameter, cm</td>
<td>100</td>
</tr>
<tr>
<td>H2</td>
<td>0.280</td>
</tr>
<tr>
<td>membrane diameter, cm</td>
<td>1.25</td>
</tr>
<tr>
<td>CH4</td>
<td>0.042</td>
</tr>
<tr>
<td>membrane thickness, cm</td>
<td>0.0005</td>
</tr>
<tr>
<td>CO</td>
<td>0.297</td>
</tr>
<tr>
<td>membrane length, cm</td>
<td>900</td>
</tr>
<tr>
<td>CO2</td>
<td>0.146</td>
</tr>
<tr>
<td>number of membrane tubes</td>
<td>3570</td>
</tr>
<tr>
<td>H2O</td>
<td>0.236</td>
</tr>
</tbody>
</table>

Simulation was performed for four different process options for hydrogen from coal gasification, as shown in Figure 13. Process A is the conventional coal to hydrogen process, where a Pressure Swing Adsorption (PSA) is used for hydrogen separation unit. Process B combines the shift reaction and hydrogen separation into a single membrane shift reactor unit. Process C is one of the membrane gasification reactor concept, where hydrogen is directly extracted from the coal gasifier and the non-permeable gas, after clean up, is used for power generation. If the non-permeable gas stream is further processed by a membrane shift reactor to increase the overall hydrogen product, this option of the membrane gasification reactor concept is designated as Process D as shown in Figure 13.
Figure 13. Comparison of Process Options for Hydrogen from Coal Gasification

For the conventional coal to hydrogen process, Process A, hydrogen recovery for the PSA unit is assumed to be 80%. The shift reaction is assumed to reach equilibrium at 250°C. If a low temperature membrane shift reactor is used as in Process B and D, the hydrogen is removed to such an extent that the partial pressure of hydrogen in the feed side is reduced to slightly above 1 atm and the shift reaction is at equilibrium. The hydrogen partial pressure in the permeate side is maintained at 1 atm, for both the membrane shift reactor and the membrane gasification reactor.

The results of the simulation are summarized in Table 4 in terms of the number of moles for the hydrogen product and the waste gas or the residual gas. The numbers in Table 4 are all normalized to the hydrogen product for the process A. Process B produces 26% more hydrogen product than Process A because Process B eliminates the hydrogen loss from the PSA tail gas and shifts more CO to H₂ using the membrane shift reactor.

Process C shows 10% improvement over the conventional process because a major amount of methane has been reformed. Significant amounts of CO still remain in the non-permeate gas from the membrane gasification reactor because the shift reaction is less favorable at higher temperatures. If the non-permeable stream is sent to a membrane shift reactor at 250°C, as in Process D, all CO can be converted to H₂ and the overall hydrogen product is 57% more than Process A. Both CH₄ and CO are reduced in Process D compared to Process A. Further, the H₂ loss in the waste stream is minimized.

The gas flows to the gas clean-up section are also listed at the bottom of the Table 4. Process C and Process D significantly reduce the gas amounts sent to the downstream clean-up section. Because Process C does not use low temperature shift reactor, additional steam is added to the gasifier for Process C so that the overall steam fed to the systems are the same for all four processes. Consequently, the amount of gas to the clean-up section for Process C is higher than Process D.

Table 4. Summary of simulation results for the four process options in Figure 13. Catalyzed reactions are assumed for the feed side of the membrane for Process C and D.

<table>
<thead>
<tr>
<th>Process</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen product, mole</td>
<td>100</td>
<td>126</td>
<td>110</td>
<td>157</td>
</tr>
<tr>
<td>Residual gas, mole</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>25</td>
<td>5</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>CH₄</td>
<td>9</td>
<td>9</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CO</td>
<td>6</td>
<td>0</td>
<td>44</td>
<td>2</td>
</tr>
<tr>
<td>CO₂</td>
<td>94</td>
<td>100</td>
<td>65</td>
<td>107</td>
</tr>
<tr>
<td>H₂O</td>
<td>26</td>
<td>20</td>
<td>47</td>
<td>4</td>
</tr>
<tr>
<td>to gas clean up</td>
<td>227</td>
<td>227</td>
<td>166</td>
<td>139</td>
</tr>
</tbody>
</table>
The simulation results confirm that the hydrogen production efficiency using the membrane gasifier process can be increased by more than 40% over the conventional gasification technology. A low temperature membrane shift reactor may be needed to work with the upstream high temperature membrane gasifier to achieve a significant improvement of the hydrogen production efficiency, as in Process D of Figure 13. The simulation also demonstrates the importance of the reaction kinetics and the thermodynamics of the gas phase reactions on affecting the membrane gasifier performance. While setting the target of the hydrogen flux for the membrane gasification reactor application, the reaction kinetics as in the methane reforming reaction, reaction equilibrium as in the shift reaction and the operating conditions as in the permeate side pressure need to be taken into consideration.

One of the major assumptions in the simulation work is that the contaminants generated from coal gasification are not considered. To address the concerns of the contaminants generated from the coal gasification on the stability of the perovskite membrane materials, Professor J. Lin of University of Cincinnati has also conducted a critical literature survey and analysis for the stability of the perovskite type ceramics under gases containing CO$_2$, H$_2$O, SO$_2$, and H$_2$S. His work covers three topics for each contaminant gas: (1) deteriorating effects on membrane surface and permeation rate, (2) poisoning mechanisms, and (3) methods to improve the chemical stability with minimized negative impacts on other properties of the material. The study will pave the way for the future work to address the stability issues of the membrane materials.

**CONCLUSIONS AND RECOMMENDATIONS**

The major achievements from this project can be summarized as follows:

- Successful fabrication of unsupported, supported and metal-containing perovskite membranes
- Development of a glass-ceramic sealing material and an improved sealing technique
- Construction of a simple and functional permeation apparatus
- Quantification of H$_2$ permeation flux through the different membranes fabricated
- Initial process evaluation for the membrane gasifier concept based on the actual hydrogen flux data
- Confirmation of the benefits of the membrane gasifier concept

Recommendations for future works include:

- Continue improving the hydrogen permeability by minimizing the membrane thickness and adding metal components to increase the electronic conductivity. Applying these two approaches to increase the hydrogen flux have been confirmed in this project. Further research will focus on these two areas.
• Scale up the size of the membrane disks. Samples as large as 1.25” diameter disks have been routinely prepared. Much bigger sizes will be needed for future commercial applications.

• Determine the membrane chemical and mechanical stability in coal derived gas atmospheres and identify approaches to address the stability issues.

• Begin conceptual design of the membrane gasifier reactor. Conduct bench scale testing for a small membrane module.

REFERENCES


DISCLAIMER STATEMENT

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