FINAL TECHNICAL REPORT
April 1, 2007, through June 30, 2008

Project Title: **DIMETHYL ETHER FROM COAL USING MEMBRANE REACTOR TECHNOLOGY**

ICCI Project Number:	06-1/5.2A-1
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ABSTRACT

The key objective of this project was to develop a novel high-temperature membrane, based on ABPBI-type (poly (2.5) benzimidazole) polymer material, for the design of a novel DME reactor system that could allow simultaneous DME synthesis and CO_2 separation. Dimethyl ether (DME: CH_3OCH_3) is a viable liquid fuel that can be produced from coal or biomass derived synthesis gas. DME is a colorless gas at room temperature and pressure, and it is a transportable liquid at about 75-80 psig, just like propane.

As CO_2 is a key reaction product for the synthesis of DME, a CO_2-selective membrane could provide several advantages related to increased syngas conversion, reduction of product gas recycle and elimination of downstream CO_2 separation.

At the end of February, 2008, we could not demonstrate sufficient experimental data for any of these ABPBI-based membranes that would indicate reasonably promising CO_2 selectivity relative to hydrogen. One key observation is that, for various short-term experiments, the ABPBI films (20-40 micron thickness) did display mechanical stability at (i) 200 psig and 260 ºC with pressure differentials of about 200 psia and (ii) one atm. pressure and 400 ºC with pressure differentials of 20-30 inches of water.

EXECUTIVE SUMMARY

This project was funded by ICCI under solicitation DCEO/ICCI RFP06-1, for the period April 1, 2007, through June 30, 2008. The key objective of the program was to develop a novel high-temperature membrane, based on ABPBI-type (poly (2.5) benzimidazole) polymer material, for the design of a novel DME reactor system that could allow simultaneous DME synthesis and CO_2 separation. Dimethyl ether (DME: CH_3OCH_3) is a viable liquid fuel that can be produced from coal or biomass derived synthesis gas. DME is a colorless gas at room temperature and pressure, and it is a transportable liquid at about 75-80 psig, just like propane. DME can be used as a multipurpose clean fuel including: as a diesel and gas-turbine fuel, as a LPG supplement and as an intermediate for the production of gasoline. Several commercial-scale plants are currently being built in several countries to produce DME from natural gas and coal.

As CO_2 is a key reaction product for the synthesis of DME, a CO_2-selective membrane could provide several advantages related to increased syngas conversion, reduction of product gas recycle and elimination of downstream CO_2 separation.

For a specific hybrid membrane made of POM-based (polyoxometalate) organic-inorganic hybrid material containing transition metal oxide clusters plus a charge-compensating organic ligand and ABPBI, preliminary experiments conducted at GTI a few years back had indicated (i) promising permeation selectivity for CO_2 relative to hydrogen and (ii) excellent chemical resistance, high glass transient temperature (~ 435 ºC) as well as good mechanical properties. These scoping experiments were conducted (i) with a feed gas containing 12% CO_2, 78% H_2 and 10% CO and (ii) at 3 psig and ambient temperature.

For the ICCI project discussed in this report, GTI researchers had postulated that a suitable membrane based on the ABPBI material only could be more effective as the presence of POM might cause dilution of the effective concentrations of the N-H functional group and thereby reduce the CO_2 selectivity from its maximum potential. Thus, for all the experimental efforts under the ICCI project, GTI researchers have used specific membranes made of ABPBI material only.

Several experiments were conducted to fabricate (i) unsupported thin ABPBI films (about 20-40 micron thick) and (ii) supported tubular membranes with ABPBI-coating on the outside surface of porous alumina (5-8 nanometer pores, 3.5 mm ID, 5.5 mm OD; bought from Media and Process Technology Inc.) and porous stainless steel tubes (micron range pores, 3.8 mm ID, 6.8 mm, 30 cm long, Pall Corporation). These membranes were primarily tested in (1) a Flat-cell reactor assembly that could operate at about 400 °C and at near one atm. pressure with pressure differentials of only about 20-30 inches of water between the feed gas and the sweep gas, and (2) a DME Synthesis Unit that could operate at about 600 °C and high pressures (~1,000 psig) with high pressure differentials. A few experiments with one specific flat (film) membrane were conducted in a different GTI bench-scale unit used usually for H_2 permeation experiments.

At the end of February, 2008, we could not demonstrate sufficient experimental data for any of these ABPBI-based membranes that would indicate reasonably promising CO_2 selectivity relative to hydrogen. One key observation is that, for various short-term experiments, the ABPBI films (20-40 micron thickness) did display mechanical stability at (i) 200 psig and 260 ºC with pressure differentials of about 200 psia and (ii) one atm. pressure and 400 ºC with pressure differentials of 20-30 inches of water. We wanted to conduct a few tests with the specific POM/ABPBI hybrid membrane which had indicated some promising CO_2 selectivity data a few years back at GTI; unfortunately, we could not locate that sample.

OBJECTIVES

The overall project objectives included: Task 1, fabricating and testing ABPBI membrane; Task 2, constructing a new DME synthesis unit using specific CO_2 selective membrane(s) based on Task 1 results; Task 3, conducting testing for DME synthesis using the Membrane Reactor; Task 4, simulation and economic analysis based on experimental results from Task 3; Task 5, project management and reporting.

INTRODUCTION AND BACKGROUND

Dimethyl ether (DME: CH_3OCH_3) is a viable liquid fuel that can be produced from coal or biomass derived synthesis gas. DME is a colorless gas at room temperature and pressure, and it is a transportable liquid at about 75-80 psig, just like propane. Because it is non-hazardous, it is currently used commercially in non-fuel applications as a propellant in perfumes and other personal care products. DME can be converted to gasoline and it can used as a gas-turbine fuel as well as a LPG supplement, and as a clean diesel fuel in diesel engines with minor retrofits, as exemplified by the operations of buses and taxis in Denmark and China. Several commercial-scale plants are currently being built in several countries to produce DME from natural gas and coal.

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For the synthesis of DME, CO_2 is a key reaction product:

- $3H_2 + 3CO = CH_3OCH_3 + CO_2$

Thus, for this specific project, it was anticipated that if a stable ABPBI-type membrane with high CO_2 selectivity relative to H_2 plus CO can be developed and used in membrane reactor for the synthesis of DME at 50-70 atm and 250-275 ºC, there could be several potential advantages related to increased syngas conversion to DME per pass, reduction of required product gas recycle, elimination of downstream CO_2 separation, and possibly, a significant reduction in the overall cost of production of DME from coal.

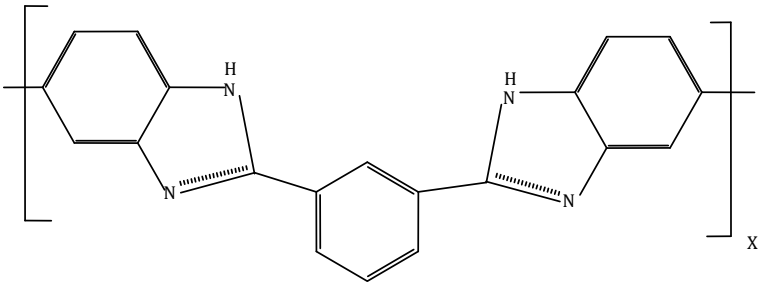
Several H_2 selective high-temperature membranes have been developed for syngas applications, such as palladium, microporous ceramic, proton conducting metal oxide, carbon molecular sieve etc. However, it is difficult to produce the so called “reverse

selective" membranes that are more selective to CO_2. While several inorganic membranes have been investigated for CO_2 separation, those are mainly tailored for CO_2 removal from flue gas or natural gas, where hydrogen is not present.[1, 2] Polymer membranes have been used successfully in various industrial applications including the production of hydrogen, nitrogen, and gas dehydration. However, current commercially available polymeric membranes are not suitable for syngas separation at high temperatures and high pressures. Usually, the membrane selectivity and flux significantly decline as the glass transition temperature of the polymer approaches.

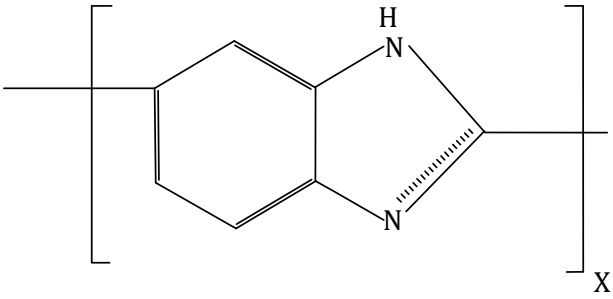
Polymeric membranes with high CO_2 selectivity relative to H_2 have been reported. Researchers from the University of Texas have developed membranes based on highly branched, cross-linked poly(ethylene oxide).[3] However, these membranes are suitable for operation at about 30-35 C. Another group at the Ohio State University has developed a polymer-based membrane, with CO_2/H_2 selectivity's greater than 100, by incorporating amine groups into polymer networks to facilitate CO_2 permeation.[4] For these membranes, though, the maximum operating temperature is below 180 °C.

GTI has been working in the area of proton exchange membrane (PEM) materials for fuel-cell applications for many years. In the area of high temperature PEMs, GTI has identified a class of polymer materials, primarily polybenzimidazole (PBI) and poly (2,5) benzimidazole (ABPBI), that show high selectivity to CO_2 permeation from gases rich in H_2 and CO at temperatures of about 400°C. Both polymers possess excellent chemical resistance, high glass transient temperature (about 435°C) and good mechanical properties. The chemical structures of these two linear polymers are shown below:

PBI



ABPBI



It seems that the presence of benzene rings in the repeating unit of the PBI molecular chain directly contributes to the polymer's superior properties. The benzene rings cause a high degree of rigidity in the polymer chain and this rigidity leads to the high glass transition temperature (Tg), which helps the polymer resist thermoplastic deformation at high temperatures. The maximum operating temperature for this polymer is quoted to be about 400 ºC. The transport mechanism for this dense, nonporous membrane is possibly based on the solution-diffusion mechanism, i.e. gas molecules first dissolve in the polymer, followed by diffusion through the membrane. The high affinity or solubility of these polymers to CO_2 derives from the N-H functional group, similar to CO_2 removal using liquid amine technology widely used in the natural gas industry.

A few years back, GTI had conducted a few scoping experiments to evaluate the possible application of a hybrid POM/ABPBI membrane that was made of: a polyoxometalate (POM)-based organic-inorganic hybrid material containing transition metal oxide clusters and a charge-compensating organic ligand was also added to the ABPBI material.[5] The membrane was coated on the interior of a porous ceramic tube. The purpose of adding the POM material was for an application not related to the ABPBI material. The test results are shown in Table 1; the feed gas (at 3 psig and ambient temperature) contained 78% H_2, 12% CO_2 and 10% CO.

Table 1: Potential of a Specific ABPBI/POM Membrane for CO_2 Permeation (Based on a Previous In-house Study at GTI)[5]

Gas composition, vol.%	Feed gas	Permeate : Test 1	Permeate : Test 2	Permeate : Test 3
$H_{2,}$	78	7.3	9.9	9.5
CO_2	12	8.5	8.1	8.1
CO	10	5.7	5.5	5.4
Methane (as Sweep Gas)	0	78.5	76.5	77.0
CO_2/H_2 selectivity*		7.7	5.3	5.5

* Selectivity: (CO_2 in permeate/CO_2 in feed)/($H_{2,}$in permeate/ $H_{2,}$in feed)

Although the material was not optimized for CO_2 separation, the data indicated promising results in terms of selectivity of CO_2 relative to H_2. Based on these past experiments, GTI researchers had postulated that the presence of POM might have diluted the effective concentrations of the N-H functional group and thereby reduced the CO_2 selectivity from its maximum potential. Thus, for this ICCI project, the efforts to develop an effective high-temperature membrane with high CO_2/H_2 selectivity were focused entirely on the ABPBI material. The project schedule, as approved by ICCI, for specific tasks is shown in Figure 1.

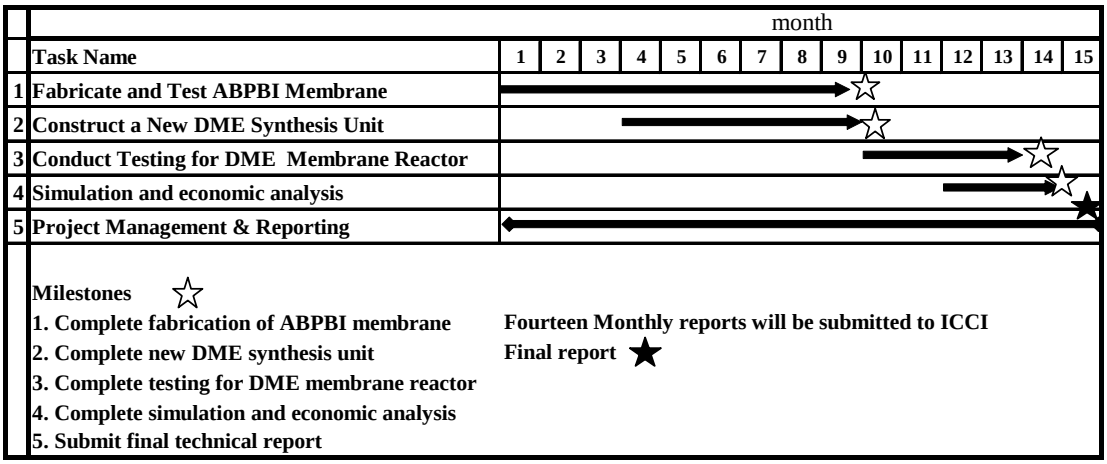


Figure 1: The Project Schedule

EXPERIMENTAL PROCEDURES

Several experiments were conducted to fabricate (i) unsupported thin ABPBI films (about 20-40 micron thick) and (ii) supported tubular membranes with ABPBI-coating on the outside surface of porous alumina (5-8 nanometer pores, 3.5 mm ID, 5.5 mm OD; bought from Media and Process Technology Inc.) and porous stainless steel tubes (micron range pores, 3.8 mm ID, 6.8 mm, 30 cm long, Pall Corporation).

These membranes were primarily tested in (1) a Flat-cell reactor assembly that could operate at about 400 °C and at near one atm. pressure with pressure differentials of only about 20-30 inches of water between the feed gas and the sweep gas, and (2) a DME Synthesis Unit that could operate at about 600 °C and high pressures (~1,000 psig) with high pressure differentials. A few experiments with one specific flat (film) membrane were conducted in a different GTI bench-scale unit used usually for H_2 permeation experiments.

RESULTS AND DISCUSSIONS

TASK 1.0: FABRICATE AND TEST ABPBI MEMBRANE

- ABPBI Membrane Preparation

The GTI Fuel Cell Group devoted considerable efforts to prepare reasonably strong and stable ABPBI based membranes (green membrane as well as ABPBI coated porous ceramic and stainless-steel tubes). The key membrane preparation methods are summarized in the following sections.

- ABPBI Solution Preparation

The poly(2,5-benzimidazole) (ABPBI) powder was purchased from Polymer Chemistry Innovations, Inc. with a batch number of 060115. The ABPBI solution was prepared by adding 2 gms of ABPBI powder to 48 gms of Trifluoroacetic acid (TF; ReagentPlux, 99%, Aldrich, batch #: 12725 JD). This 1:24 weight ratio (ABPBI: TF) was found to be an optimum ratio for maximizing the level of ABPBI in the overall solution; by adding more ABPBI powder, we could not obtain homogeneous solution. We then added 2 gms of phosphoric acid (PA: H_3PO_4; as 85 wt% aqueous solution, Aldrich, batch #: 7664-38-2) to this ABPBI/TF solution; the actual H_3PO_4 level was thus 1.7 gms. . The PA was added to enhance smooth preparation of the green membranes during the “tape casting” process; TF is relatively more volatile than PA, and we had observed that without the presence of the PA, the ABPBI solution in TF would vaporize quite rapidly and it was difficult to obtain uniformly thick membrane films. The ABPBI/TF/PA mixture was sealed and stirred until homogenous solution was formed.

- Unsupported Membrane Fabrication

Unsupported ABPBI membrane films were prepared by the tape casting method (a schematic is shown in Fig .2). The ABPBI solution was distributed evenly onto a flat horizontal surface by means of a blade to prepare green membrane films (typically, 20-40 microns thick). These green membrane films were then (i) air-dried at ambient temperatures in a laboratory hood for about 12 hours and (ii) then placed in a 0.1 M NaOH solution for 24 hours to neutralize any excess acid on the ABPBI films. Finally, these membrane films were washed with distilled water at room temperature and were stored in distilled water (Figure 3) to ensure that there was no residual NaOH in these membranes. Before permeation measurement using green membranes films, these were dried in an oven at a temperature of 50ºC for about 10 minutes. A 6 inch x 15 inch ABPBI film is shown in Figure 4.

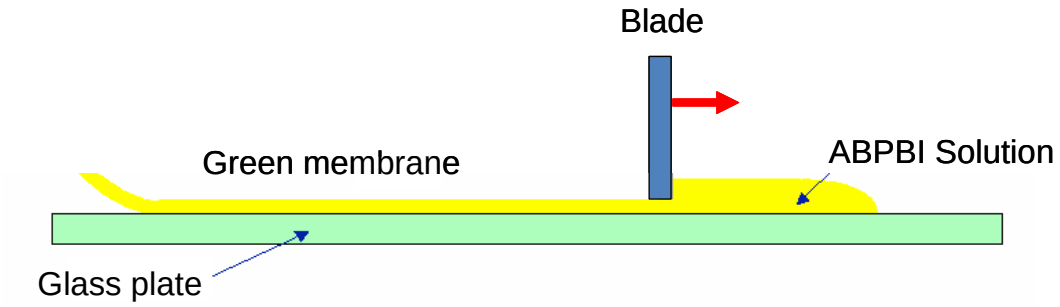


Figure 2: Schematic Diagram of “Tape Casting”

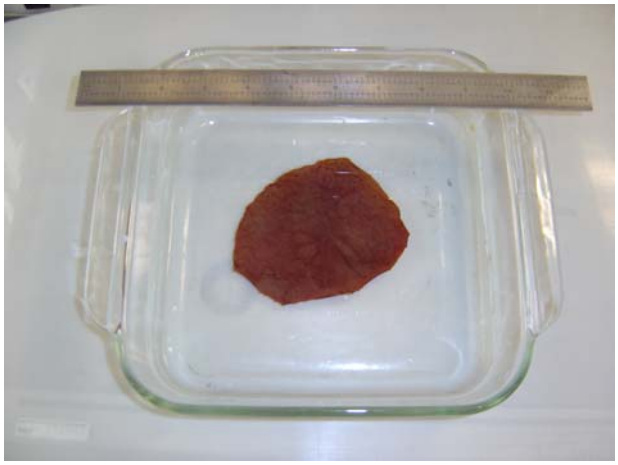


Figure 3: An ABPBI Membrane Stored In Water

Figure 4: A 6 inch x 15 inch ABPBI Film (about 20 micron thick)

- Supported Membrane Fabrication

We used the same ABPBI/TF/PA solution mentioned above to fabricate tubular membranes with ABPBI-coating on the outside surface of specific porous alumina (5-8 nanometer pores, 3.5 mm ID, 5.5 mm OD, Media and Process Technology Inc.) or porous stainless steel tubes (micron range pores, 3.8 mm ID, 6.8 mm, 30 cm long, Pall Corporation). Non-porous stainless steel tubes (2.5 cm long) were welded onto each end the stainless steel supports. Before synthesis, the supports were boiled in distilled water for 1 hour and dried at 100 for about 30 minutes.

The bottom end of the support was plugged with Teflon tape before coating. The dip-coating process was carried out as follows: the vertical tubes were first dipped in the ABPBI solution for 2 minutes, then withdrawn vertically at a slow rate, and finally natural dried in the hood for 1 h. The color of the outside surface turned into yellow after coating. To ensure the outside surface was completely covered with ABPBI, a second-layer coating was applied using the same procedure mentioned above.

Similar to the unsupported membrane, the supported membranes were placed in a 0.1 M NaOH solution for about 40 hours. Then, the membrane was washed with distilled water and stored in the hood. Figure 3 shows the picture of the porous alumina support and the ABPBI membrane coated on the outside surface.

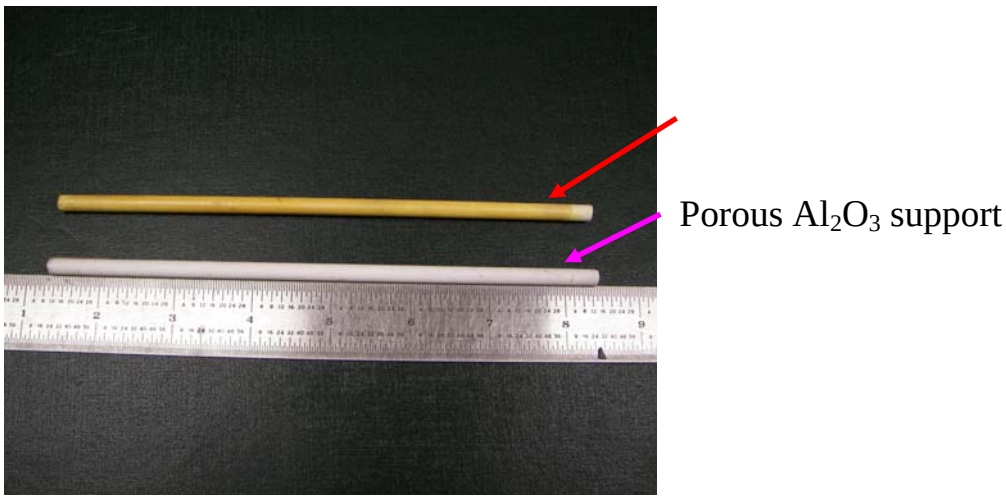


Figure 5: Picture of a Porous Alumina Support & an ABPBI Membrane Coated on the Outside Surface.

- Various Experiments under Task 1

Under Task 1, various experiments were conducted to (i) test the mechanical integrity of various types of membranes that were prepared and (ii) modify the membrane preparation techniques. Most of these tests involved flat ABPBI membrane films using a "Flat Cell Reactor" assembly shown in Figure 6. This reactor could be operated at (i) only near atmospheric pressure and with a pressure differential of about 20-25 inches of water, and (ii) at temperatures of about 400 ºC. The "bench-scale permeation measurement experimental unit" is shown in Figure 7. The key studies included:

- Preparation of specific ABPBI solutions to determine suitable viscosity ranges that would be appropriate for coating alumina ceramic tubes.
- Experiments to measure "porosity" of ceramic and stainless-steel tubes.
- Leak tests in the Flat Cell Reactor (based on gas flow rates in the feed gas side and sweep gas side of the reactor).
- Specific CO_2 flux measurements.

a. Flat-cell Testing

The key test procedures involve: (i) assembling the membrane in the test reactor, (ii) leak testing at room temperature, and (iii) heating to 400^{o}C for further leak and permeation tests. The membrane samples had thickness of about 20-40 microns. During the initial experiments, we had observed (i) significant cross-leakage across the flat membrane films and (ii) damage to the films, especially along the seal edges (as shown in Figure 8).

These problems were solved after many trials in the preparation of suitable membrane films and with suitable design of the reactor seals.

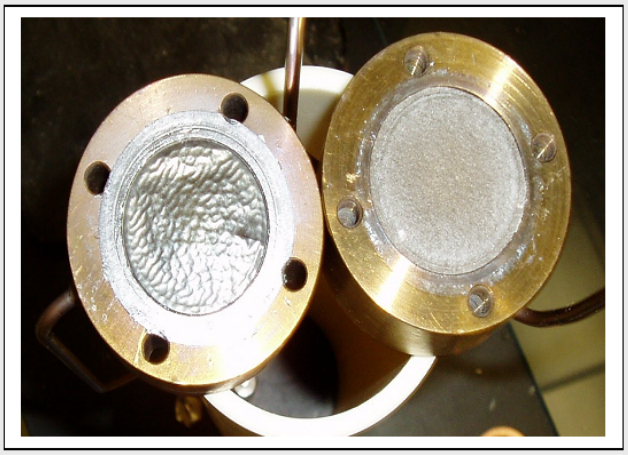


Figure 6: Flat Cell Reactor Assembly

(The Left Chamber was for the sweep gas and the right for feed gas)

Figure 7: Bench-scale CO_2 Flux Measurement Unit (for operations at near 1 atm.)

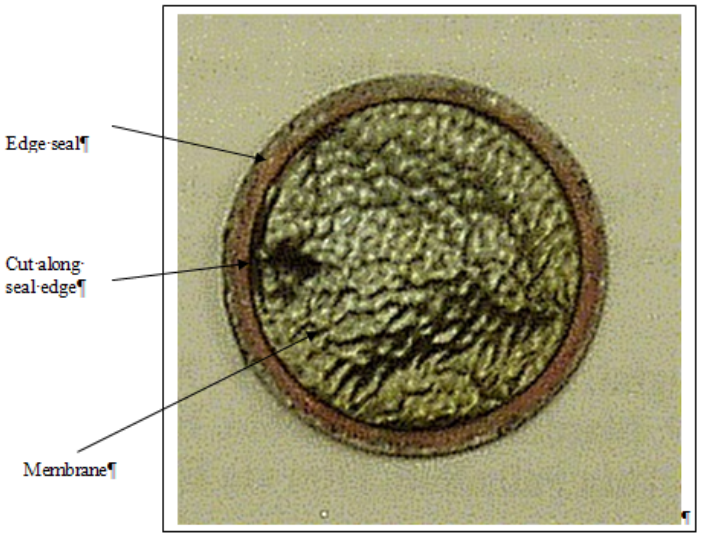


Figure 8: Typical Example of Post-Test Damaged Membrane

b. Flux Measurements

We were not successful in obtaining meaningful CO_2 permeation data using this low-pressure Permeation Test Reactor system. Typical flux measurement data that indicate insignificant CO_2 flux are shown in Table 2:

Table 2: Typical CO_2 Flux Measurement Data Measured Using the Flat Cell Reactor

Test Condition	CO_2 Flux (std. cc/minute)
Background CO_2 concentration	0.01-0.02
CO_2 Feed/Nitrogen Sweep, 400 °C	0.01-0.02
CO_2 + 20 % Water Vapor/Nitrogen Sweep, 400 °C.	0.02
CO_2 + 20 % Water Vapor/Nitrogen Sweep at near 1 Atm. pressure & 400 °C, and a Differential Pressure of 21 inches water	0.02

TASK 2.0: CONSTRUCT A NEW DME SYNTHESIS UNIT

Under Task 2, GTI built a laboratory-scale DME Synthesis Unit (DSU) for integrated testing of DME synthesis and CO_2 permeation. The design of this unit is based on the fixed-bed reactor concept and the tubular membrane geometry. The unit can be operated at a pressure of 1,000 psig and a temperature of about 600 ºC. The primary reactor section is shown schematically in Figure 9.

The central tube (which would be an ABPBI-coated membrane tube, made of either ceramic or porous stainless steel tube) would perform like a membrane to remove CO_2 from the annular reactor section (with an outside diameter of about 1 inch) which would be filled with a suitable DME synthesis catalyst. Synthesis gas (a mixture of hydrogen and CO) would be fed through the "feed inlet" port and the product gases (primarily DME, methanol, water vapor, CO_2 and unconverted synthesis gas) would exit through the feed outlet port. A suitable "sweep gas" (e.g. nitrogen) would be fed through the sweep gas in port and the mixture of the sweep gas + some CO_2 (that would be permeating through the membrane) from the annular reactor section would leave the membrane tube through the sweep gas out port.

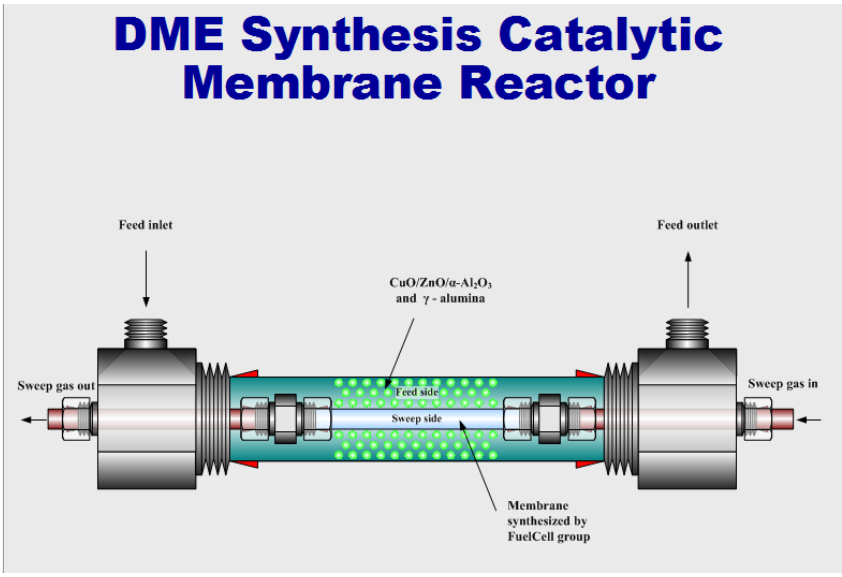


Figure 9: Schematic of the Reactor section in the DME Synthesis Unit

A simplified schematic of the experimental setup is shown in Figure 10, and a picture of the reactor system with associated GC equipment plus control systems is shown in Figure 11.

The outlet section of the reactor unit was wrapped by heating tapes to prevent condensation of the product liquids. This DSU system and the associated piping were tested for leak at about 500 psig and at a temperature of about 500 ºC. For the CO_2 permeation tests with tubular membranes, successful sealing was provided by "graphite ferrules".

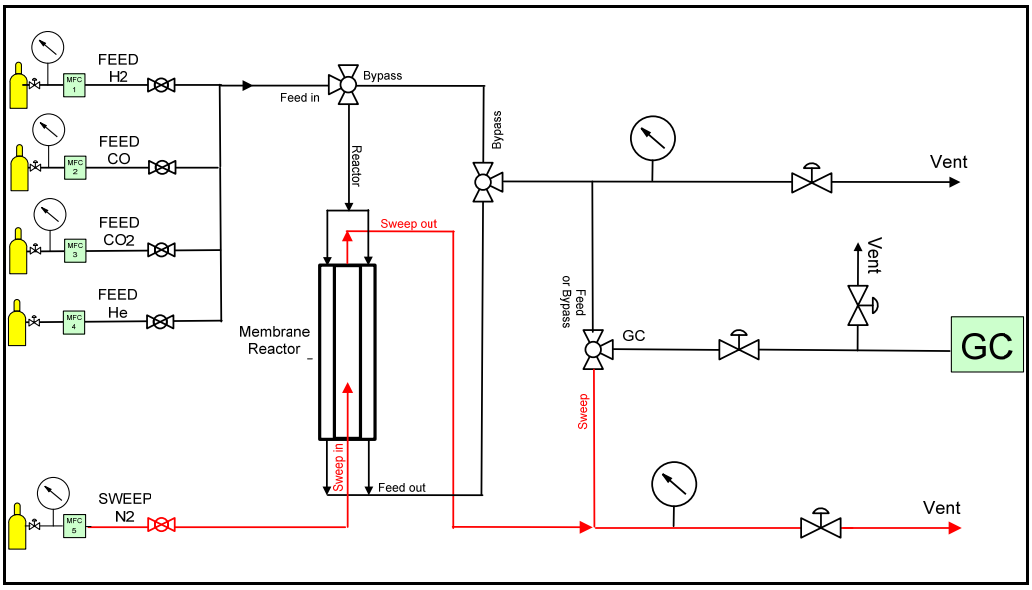


Figure 10: Schematic of the DME Synthesis Unit

Figure 11: The Bench-scale DME Synthesis Unit

TASK 3.0: CONDUCT TESTING FOR DME SYNTHESIS USING MEMBRANE REACTOR

As noted before, under Task-1 on the fabrication and testing of ABPBI membranes, we could not perform any CO_2 permeation tests at relatively high pressures (vis-à-vis a typical pressure of 50-70 atm required for DME synthesis) and high pressure differentials. Thus, when the DSU became operational under Task 2 objectives, we had decided to first generate specific experimental data (at relatively high pressures and high pressure differentials) on the extent of CO_2 permeation for the specific ABPBI-based membranes that the GTI Fuel Cell Group had fabricated for testing under the Task 3. Although we had procured specific catalysts for methanol synthesis (Katalco 51-9 from Johnson Matthey Co.) as well as for methanol dehydration (gamma-alumina from Alfa-Aesar) for the synthesis of DME, we did not have clear indications that we could fabricate stable ABPBI-membranes that could provide significant CO_2/H_2 selectivity under the DME synthesis process conditions.

Under Task 3, we had conducted the following CO_2 permeation tests using:

- One ABPBI-coated Stainless Steel tubular membrane (shown in Figure 12) in the DSU

- One ABPBI-coated Ceramic tubular membrane (shown in Figure 13) in the DSU

- One flat ABPBI membrane film (20 micron thick) was tested in a separate GTI laboratory unit used in-house for performing hydrogen permeation experiments.

For these tests, we had used a 50/50 gas mixture of CO_2 and Helium at various pressures with nitrogen as the sweep gas. The experimental data on these tests are given in Table 3.

- Stainless Steel Membrane

The pressure testing using laboratory air (at about 60 psig) indicate that the ABPBI-coated SS membrane was not "dense" at room temperature. The CO_2/He experiments (at ambient temperature & at 250^oC) with this SS membrane indicate no CO_2 selectivity relative to Helium. As we could not achieve a differential pressure (delta-P) value of higher than 5 psi, we believe that that pores of the SS support are not completely closed, and this resulted in CO_2 and He permeation through open pores rather than through the APBPI film. It could possibly be beneficial to increase the extent of ABPBI coating thickness for extensive "closing" of these pores and thereby, to achieve a CO_2-selective membrane.

- Ceramic membrane

The experimental data (for a Temperature range of ambient to 250^{o}C & delta-P of about 9-45 psi) using the ceramic tubular membrane also indicate no CO_2 selectivity. Although the pores of this ceramic membrane are "smaller" relative to those for the membrane on the stainless steel support, it appears these pores are not completely closed. Preferential permeation of helium is explained by the conventional "Knudsen diffusion" mechanism. Under this diffusion mechanism, selectivity of gases would depend on the "square root" of ratio of the molecular weights of gases involved; smaller molecules would permeate more than the bigger molecules. Again, it is possible that additional thicker "ABPBI coating" could be helpful to achieve a CO_2-selective membrane for such ceramic supports.

- Flat ABPBI Membrane

A flat membrane (~ 20 micron in thickness) was cut from a ABPBI membrane sheet synthesized by the Fuel Cell group. This membrane was placed on the top of a porous stainless steel disk (pore size: about 10 microns). As shown in Table 3, for a gas mixture of 50% CO_2/50% He, this membrane showed no CO_2 and He permeation up to a temperature of about 100ºC with delta-P values of about 2-50 psi. When the temperature was increased to about 200ºC, small amounts of CO_2 and He permeation were observed, but the helium flux is much bigger than the CO_2 flux. This membrane could possibly have some pores, and some CO_2 transport could occur through these pores rather than through the ABPBI film. As compared with the membranes deposited on ceramic and SS tubular supports, this flat membrane could have some smaller voids that possibly resulted in no CO_2 selectivity. At this point, we can only hypothesize that that the use of relatively thicker flat membranes or the use of significantly more concentrated solution of the ABPBI material during the synthesis step could possibly produce a dense membrane for use at high temperatures and pressures.

These CO_2/He permeation experiments indicate that more "dense" membrane should be synthesized so that there would be no gas diffusion through pore openings, and the main gas transport would occur through a "solution-diffusion" mechanism where the concept of a "preferential" CO_2 permeation could possibly work.

Figure 12: ABPBI-coating on Porous Stainless-steel Membrane.

Figure 13: ABPBI-coating on Ceramic Porous Support.

Table 3: Results of Permeation Experiments using the DME Synthesis Unit

Membrane	Feed pressure, psig	Pressure difference, psi	Temperature, ^{o}C	Feed composition	Permeate composition,%	
					CO_2	He
SS tubular membrane	9	3	Room	50%CO_2/50%He	44	56
	11	5	250	50%CO_2/50%He	45	55
Ceramic membrane #1	15	9	Room	50%CO_2/50%He	38	62
	15	10	100	50%CO_2/50%He	37	63
	20	15	200	50%CO_2/50%He	33	67
	20	15	250	50%CO_2/50%He	32	68
	50	45	250	50%CO_2/50%He	41	59
Flat membrane #1 **	3	3	Room	50%CO_2/50%He	0	0
	2	2	100	50%CO_2/50%He	0	0
	25	25	100	50%CO_2/50%He	0	0
	50	50	100	50%CO_2/50%He	0	0
	50	50	200	50%CO_2/50%He	6	94
	100	100	260	50%CO_2/50%He	7	93
	200	200	260	50%CO_2/50%He	7	93

** These tests were conducted at the bench-scale unit used for hydrogen permeation experiments at GTI

Cancellation of (i) Additional Tests under Task 3 and (ii) Task 4

At the end of February, 2008, we could not demonstrate sufficient experimental data for any of the GTI-fabricated ABPBI-based membranes that would indicate reasonably promising CO_2 selectivity relative to hydrogen. Without such a membrane, we did not want to conduct any experiments involving DME synthesis although we had built a high-pressure DME Synthesis Reactor and had procured suitable methanol synthesis as well as methanol dehydration catalysts.

We wanted to conduct a few tests with the specific POM/ABPBI hybrid membrane which had indicated some promising CO_2 selectivity data a few years back at GTI; unfortunately, we could not locate that sample.

CONCLUSIONS AND RECOMMENDATIONS

Our key conclusions are:

- We could not fabricate any ABPBI-based membrane that indicated reasonably promising CO_2 selectivity relative to hydrogen.

- One key observation is that, for various short-term experiments, a few ABPBI films (20-40 micron thickness) did display mechanical stability at (i) 200 psig and 260 ºC with pressure differentials of about 200 psia and (ii) one atm. pressure and 400 ºC with pressure differentials of 20-30 inches of water.

In case ICCI would like to work with GTI in further pursuing the potential of ABPBI-based membranes in selectively separating CO_2 from a mixture of gases containing hydrogen and CO, we would recommend:

- Exploring the potential of hybrid membranes made of POM-based (polyoxometalate) organic-inorganic hybrid material containing transition metal oxide clusters plus a charge-compensating organic ligand and ABPBI; preliminary experiments conducted at GTI a few years back had indicated (i) promising permeation selectivity for CO_2 relative to hydrogen and (ii) excellent chemical resistance, high glass transient temperature (~ 435 ºC) as well as good mechanical properties for this type of hybrid membranes.

Initial tests should involve :

- Fabrication of thin membrane films (of various thicknesses).

- CO_2 permeation experiments using the high-pressure DME Synthesis Unit or the GTI bench-scale unit used typically for hydrogen permeation experiments. Both of these units are capable of operating at reasonably high temperatures as well as high pressures and with relatively high differential pressures.

- Initial “permeation” experiments should be conducted using gas mixtures containing 50% CO_2 and 50% helium (or hydrogen) to determine if there is any selective CO_2 permeation.

- If any such thin membrane films made of ABPBI or ABPBI/POM materials indicate promising CO_2 selectivity data, the efforts should then be focused on fabricating tubular membranes with coatings of such ABPBI or ABPBI/POM hybrid materials.

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