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Texas Commission on Environmental Quality
New Technology Research & Development (NTRD) Program
Monthly Project Status Report

Contract Number: 582-5-65591-0002 .

Grantee: The University of Texas at Austin .

Date Submitted: June 30, 2006

Report for the **Monthly** period:

Starting Date: April 1, 2006 Ending Date: April 30, 2006

Section I. Accomplishments (*Please provide a bulleted list of project accomplishments as well as a description of their importance to the project.)*

PROJECT OBJECTIVES

The overall objective of this project is to develop cost-effective, high-temperature gas separation membranes for producing inexpensive, high-purity hydrogen (H_2) from synthesis gas generated by steam reforming or gasification of fossil fuels. The two specific technical objectives of the project are:

(i) To develop polymeric and/or polymer-based nanocomposite membranes with high H_2 permeability, high H_2/carbon monoxide (CO) and H_2/carbon dioxide (CO_2) selectivities, and high thermal stability up to 250-300 °C.

(ii) To demonstrate the technical and economic feasibility of using such membranes for producing low-cost fuel-cell-quality H_2 from synthesis gas streams.

PROJECT ACTIVITIES AND STATUS

The Grant Activities for the project consist of seven (7) tasks. The project accomplishments during this report period are summarized in the bulleted list below.

UT

- UT has completed all tasks.

RTI

- Membrane Permeation Testing: Evaluation of the gas permeation properties of the tubular PBI (polybenzimidazole) composite membrane module was completed. The module was tested at 250 and 300 °C up to 300 psig feed pressure with pure H_2 and CO_2 and a three-component syngas mixture. ***(Project Task 2)***

- Integrated System Process Design: Simulations began for using the high-temperature PBI membrane module as a membrane reactor for conducting water gas shift (WGS) reaction with simultaneous hydrogen separation. The process conditions for the synthesis gas produced (e.g., stream flow rate, stream composition, pressure, temperature, desired hydrogen stream flow rate and purity, etc.) by the natural gas autothermal reforming process were established. ***(Project Task 5)***

Specific results and details of this period's project activities are discussed on a task-by-task basis below.

Indicate which part of the Grant Activities as defined in the grant agreement, the above accomplishments are related to:

TASK 1: Prepare High-Temperature Membranes

UT

This task has been completed.

RTI

This task has been completed.

TASK 2: Evaluate Membrane Permeation Properties

UT

This task has been completed.

RTI

Previously, the pure- and mixed-gas permeation properties of the tubular PBI composite membrane module (apparent PBI layer thickness ~ 0.65 µm; effective membrane area ~ 28.4 cm^2) from Pall Corporation had been determined from 20 to 200 °C as a function of feed pressure. This period, to complete the temperature and feed pressure dependence studies on this module, its permeation properties were measured at the higher temperatures of 250 and 300 °C with pure H_2 and CO_2 and the ternary syngas mixture (36.8% H_2, 12.5% CO_2, and 50.7% CO) up to feed pressures of 300 psig.

Figures 1 and 2 present the pure- and mixed-gas selectivities and permeabilities, respectively, obtained for PBI Module #2 at 250 and 300 °C. Similar to last month for the experimental feed pressure range studied, the mixture H_2/CO selectivity values of PBI Module #2 only vary somewhat for the two highest temperatures studied in this characterization. As shown in Figure 1, the H_2/CO selectivity values are about 47-58 at 100 psig and 37-52 at 300 psig over the 250-300 °C temperature range. These values are roughly 13-40% lower than the H_2/CO selectivities obtained last period at the lower temperatures of 150 and 200 °C. As mentioned in previous reports, this selectivity decline for increasing feed pressure is due to the CO permeability increasing more quickly with increasing feed pressure than the H_2 permeability (cf. Figure 2). It was also noted previously that the pressure dependence of the H_2/CO selectivity appeared to be weaker at higher temperatures than at lower temperatures [i.e., observed selectivity reduction of ~10% at 250 °C (this report) and 15-16% at 150 and 200 °C (cf. March monthly report) versus 30-36% at 20 and 100 °C (cf. January and February 2006 monthly reports)]. However, at 300 °C, the observed selectivity reduction is higher at ~21%, the possible cause of which is described below.

Relative to the H_2/CO selectivity, the H_2/CO_2 selectivity continues to exhibit consistently less dependence on feed pressure. As discussed in last month's report, over the feed pressure range of 100-300 psig, the H_2/CO_2 selectivity is nearly constant at ~21-22 for 150 °C and ~22-25 for 200 °C. This trend continues into the higher experimental temperatures investigated this month, yielding H_2/CO_2 selectivity values of 22-24 at 250 °C and 19-21 at 300 °C. Although the selectivity values measured under pure- and mixed-gas conditions are very similar at the higher temperatures from 150 to 300 °C, the H_2/CO_2 selectivity usually tends to lie at the lower end of these selectivity ranges under mixed-gas

conditions mainly because the mixture CO_2 permeability is somewhat higher than that obtained under pure-gas test conditions. The H_2 permeability stays essentially constant for the pure-gas and syngas mixture test conditions over the entire experimental pressure range and is roughly 6.9-7.4 barrers at 250 °C and 10-11 barrers at 300 °C (cf. Figure 2).

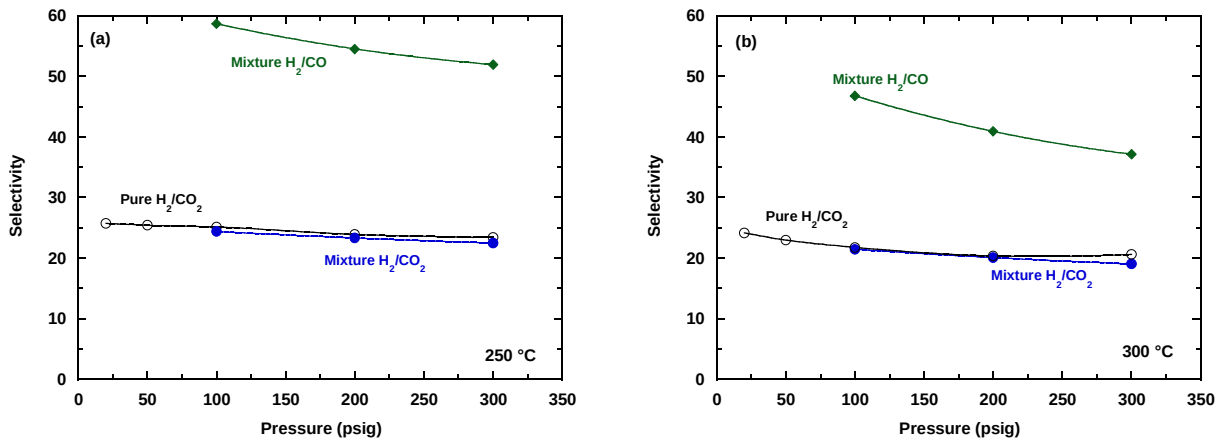

Figure 1. Effect of feed pressure on pure- and mixed-gas selectivities in tubular, AccuSep-supported, PBI membrane module #2 at (a) 250 °C and (b) 300 °C. Selectivities were computed from permeability data shown in Figure 2. Mixture tests were performed with an industrially representative ternary syngas of 36.8% H_2, 12.5% CO_2, and 50.7% CO. Permeate pressure = 0 psig; Downstream He sweep rate = 20 cm^3/min. 1 barrer ≡ 10^{-10} cm^3(STP)·cm/(cm^2·s·cmHg).

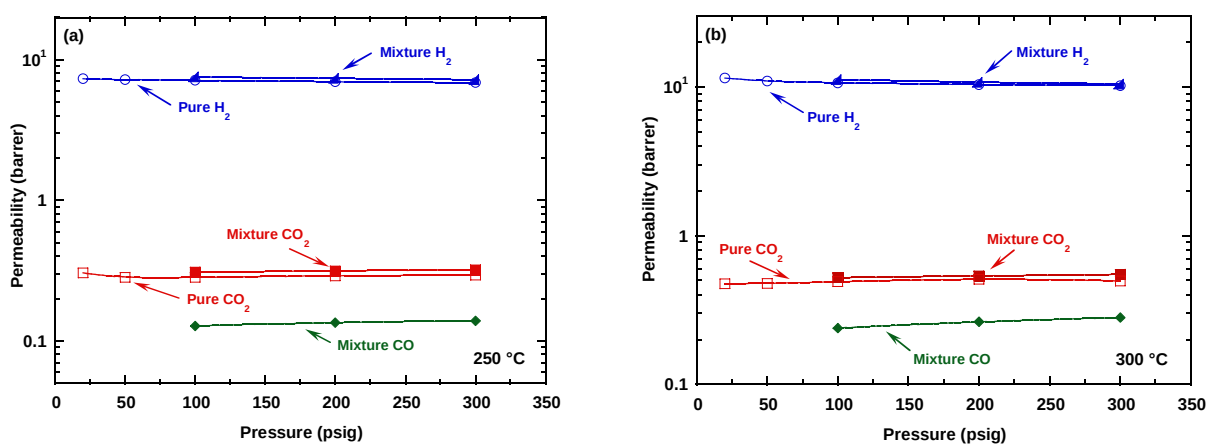

Figure 2. Effect of feed pressure on pure- and mixed-gas permeabilities in tubular, AccuSep-supported, PBI membrane module #2 at (a) 250 °C and (b) 300 °C. Experimental conditions are given in Figure 1 caption.

Table 1 provides a data summary of the representative impact of temperature on PBI module separation performance. Raising the temperature from 20 to 200 °C substantially improves module separation properties, leading to a 4- to 7-fold increase in H_2/CO_2 selectivity and a 16- to 17-fold increase in H_2/CO selectivity. This behavior could be attributed to the effect of temperature on diffusion and solubility selectivities. The kinetic diffusivity component to gas permeability is an activated process, and raising temperature would increase diffusion rates of H_2, CO_2, and CO in PBI. An increase in polymer chain mobility (and, hence, polymer free volume) would also accompany the temperature elevation, thus potentially making the polymer less able to discriminate between different gases on the basis of molecular

size (i.e., lowering diffusivity selectivity). On the other hand, the solubility component to permeability favors larger, more condensable molecules such as CO_2 over the smaller, less soluble molecules such as H_2. However, a temperature increase generally results in a decrease in gas solubility. Thus, to effect the observed significantly higher H_2/CO_2 selectivity at the higher temperatures, the decrease in CO_2 solubility should be substantially greater than the increase in CO_2 diffusivity with increasing temperature. In the case of H_2, the diffusion component for this light gas would dominate its permeation behavior, especially at higher temperatures. Consequently, overall permeability increases much more rapidly for H_2 than for CO_2, resulting in the better H_2/CO_2 selectivity seen as temperature increases to 200 °C. A similar argument could also be made for the temperature dependence of the H_2/CO selectivity. As temperature increases above 200 °C, the H_2/CO and H_2/CO_2 selectivities start to diminish slightly but are still significantly higher than those at 20 °C. This behavior suggests that the diffusion components for all gas species, particularly the larger CO and CO_2 species, is playing an increasingly greater role above 200 °C (i.e., the decreased size-sieving ability of the polymer matrix at higher temperature is becoming gradually more dominant).

Table 1. Comparison of Pure- and Mixed-Gas Selectivity Data Obtained over Temperature Range of 20-300 °C for Tubular PBI Composite Membrane Module #2

Temperature (°C)	H_2/CO selectivity[a]	H_2/CO_2 selectivity[a]	
	In syngas[b]	In pure gas	In syngas[b]
20	4.0	5.8	3.3
100	42	19	16
150	67	22	21
200	65	26	23
250	55	24	23
300	41	22	20

[a] Determined at 200 psig feed pressure.

[b] Syngas mixture composition of 36.8% H_2, 12.5% CO_2, and 50.7% CO.

Upon completion of the comprehensive characterization for gas permeation properties of the tubular PBI composite membrane module for temperature and pressure, an H_2S-containing syngas mixture was used to evaluate the membrane module from 100 to 300 psig at 300 °C. After the 100 psig test, pure H_2 and CO_2 were checked to ensure that H_2S had not adversely affected the membrane module, and post-pure-gas checks were also completed after the full pressure characterization was finished. Figure 3 compares the permeation properties obtained with the H_2S-containing syngas mixture to those measured with pure H_2 and CO_2 and the non-H_2S-containing, ternary syngas mixture. H_2S did not permeate through the membrane until 300 psig. The H_2/H_2S and CO_2/H_2S selectivities were calculated to be 80 and 4.3, respectively, at 300 °C.

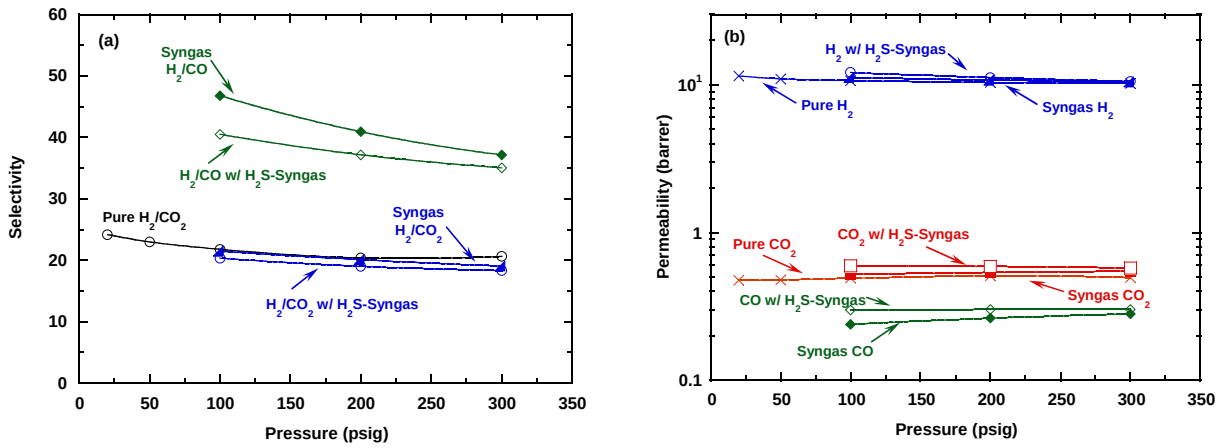

Figure 3. Effect of feed pressure on pure- and mixed-gas (a) selectivities and (b) permeabilities in PBI membrane module #2 at 300 °C. Selectivities were computed from permeability data shown in Figure 3b. Mixture tests were performed with a ternary syngas (36.8% H_2, 12.5% CO_2, and 50.7% CO) and a four-component, H_2S-containing syngas (1.02% H_2S, 35.9% H_2, 13% CO_2, and 50.08% CO). Permeate pressure = 0 psig; Downstream He sweep rate = 20 cm^3/min. 1 barrer ≡ 10^{-10} cm^3(STP)·cm/(cm^2·s·cmHg).

TASK 3: Evaluate Membrane Reactor Properties

RTI

This task could not be performed because PBI nanocomposite membranes doped with catalytic nanoparticles active for water-gas-shift or hydrogenation have not stayed defect-free long enough to warrant evaluation of their membrane reactor properties. Rather the water vapor permeability obtained at 150, 225, and 265 °C in an earlier study in unfilled PBI will be used to simulate a water-gas-shift membrane reactor process in which shift catalyst is packed outside the PBI membrane (cf. Task 5).

TASK 4: Characterize Thermal and Morphological Properties of Membranes

UT

This task has been completed.

RTI

This task has been completed.

TASK 5: Prepare Integrated System Process Design

RTI

During this period, the process conditions for the synthesis gas produced (e.g., stream flow rate, stream composition, pressure, temperature, desired hydrogen stream flow rate and purity, etc.) by the natural gas autothermal reforming process were established. The high temperature PBI membrane module may be used as a membrane reactor for conducting water gas shift (WGS) reaction with simultaneous hydrogen separation or simply as a hydrogen separation unit after conducting the water gas

shift reaction in a conventional low temperature reactor. A possible advantage of using the membrane module as a membrane reactor is to increase the yield of hydrogen in the equilibrium limited WGS reaction by removing one of the reaction products. Membrane module simulations were therefore conducted both in the active membrane reactor mode as well as in the passive separation mode following a conventional reactor to determine hydrogen yield, permeate and residual gas compositions, and membrane area for a designated hydrogen recovery. Mixed gas membrane permeability for H_2, CO, and CO_2, determined using a PBI/AccuSep composite membrane module provided by Pall Corporation was used in the simulations. These data included membrane permeability for H_2, CO, and CO_2, at temperatures up to 300 °C, and pressure up to 300 psig pressure. Since PBI is highly permeable for water vapor, water permeability and selectivity data collected using PBI films in an earlier study were also used in the model simulations.

Membrane module simulations were conducted using representative synthesis gas compositions resulting from an autothermal reforming process at 100 psig pressure. The synthesis gas was assumed to be cooled to 300 °C temperature and mixed with additional steam to adjust the steam to CO ratio to a designated value chosen as a model parameter. Simulations were conducted both in the active and passive modes for steam to CO ratios of 1:1, 1.5:1, and 2:1 for a net hydrogen recovery of 80% in the membrane module. Since PBI membrane is more permeable to water vapor than for hydrogen, using the membrane module as a membrane reactor did not indicate any increased CO conversion as any advantage of product hydrogen separation was offset by separation of water reagent as well. For a given steam to CO ratio, the membrane area requirements for net 80% hydrogen recovery were similar for both active and passive mode operations with a slightly lower area needed in the passive mode. Increasing steam to CO ratio increased the equilibrium CO conversion and hydrogen concentration resulting in a decrease in membrane area requirement likely to be leveling off at a greater steam to CO ratio. All simulations indicated permeate hydrogen concentration in the range of 90 to 93% (dry basis) for a net hydrogen recovery of 80%. Further purification of the product hydrogen stream will be necessary to condense out water and to remove CO before using the hydrogen in a PEM fuel cell. Additional simulations are being conducted and a process design to produce 10 L/min hydrogen is being developed.

TASK 6: Perform Technical and Economic Analysis/Develop Commercialization Strategy

RTI

This task has not yet started.

TASK 7: Manage Project/Prepare Reports

UT/RTI

The fifteenth monthly project report was prepared.

Section II: Problems/Solutions

Problem(s) Identified (*Please report anticipated or unanticipated problem(s) encountered and its effect on the progress of the project)*	UT No major problems were encountered this period. RTI No major problems were encountered this period.

Proposed Solution(s) *(Please report any possible solution(s) to the problem(s) that were considered/encountered)*	UT N/A this period. RTI N/A this period.
Action(s) Conducted and Results *(Please describe the action(s) taken to resolve the problem(s) and its effect)*	UT N/A this period. RTI N/A this period.

Section III. **Goals and Issues for Succeeding Period**: (*Please provide a brief description of the goal(s) you hope to realize in the coming period and identify any notable challenges that can be foreseen)*

UT

All tasks are completed. No further experiments are necessary.

RTI

Next month, development of a process design integrating a high-temperature membrane separation step to produce 10 L/min hydrogen will continue as additional simulations will be conducted. Detailed written report drafts for completed project tasks will also be prepared.

Benny Freeman

_____. Date: June 30, 2006 .

Authorized Project Representative's Signature

NOTE*: Please attach any additional information that you feel should be a part of your report or that may be required to meet the deliverable requirements for tasks completed during this reporting period.*