CO₂ SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS-SHIFT REACTION WITH CONCOMITANT RECOVERY OF CO₂

Quarterly Report For the period October 1, 2003 to December 31, 2003

> Paul K. T. Liu Project Director

February 19, 2004

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY Under Cooperative Agreement No. DE-FC26-00NT40922

By MEDIA AND PROCESS TECHNOLOGY, INC. 1155 William Pitt Way Pittsburgh, PA 15238

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Two process schemes have been investigated by us for the use of hydrotalcites we prepared as CO₂ adsorbents to enhance water gas shift (WGS) reaction: Case I involves the adsorption enhanced WGS packed bed reactor and Case II involves the adsorption enhanced WGS membrane reactor. Both cases will achieve the same objective as the hydrotalcite membrane reactor: i.e., improving the WGS reactor efficiency via the concomitant removal of CO_2 for sequestration. In this report a detailed investigation of the design characteristics and performance of Case II, termed the Hybrid Adsorbent-Membrane Reactor (HAMR), is presented. The HAMR system includes a packed-bed catalytic membrane reactor (hydrogen selective) coupling the WGS reaction (in a porous hydrogen selective membrane) with CO₂ removal with an adsorbent in the permeate side. The reactor characteristics have been investigated for a range of permeance and selectivity relevant to the aforementioned application. The HAMR system shows enhanced CO conversion, hydrogen yield, and product purity, and provides good promise for reducing the hostile operating conditions of conventional WGS reactors, and for meeting the CO_2 sequestration objective. In the next quarterly report we will present the simulation result for Case I as well as the progress on hydrotalcte membrane synthesis.

TABLE OF CONTENTS

1.	Introduction
2.	Executive Summary1
3.	Experiment1
4.	Results and Discussion
5.	Conclusions

List of Graphical Materials Figures

Figure 1	Schematic diagram of a packed bed membrane reactor	8
Figure 2	CO conversion vs. reactor length for catalytic membrane packed bed reactors.	
	T(C)=275, Por(atm)=1, ST sec=10,SR=0.25, Perm=1.0x10 ⁻⁶ mole/(cm ² -sec-	
	atm),H ₂ /CO=100, CO ₂ /CO=1	14
Figure 3	Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed	
	reactors. (Conditions same as in Figure 1)	15
Figure 4	Hydrogen Recovery (%) in catalytic Membrane Reactor (conditions same as in	
	Figure 1)	16
Figure 5	Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in	
	membrane along the Membrane Side (conditions same as in Figure 1)	16
Figure 6	CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors.	
	T(C)=275, Por(atm)=7.8027, Pom(atm)=1, ST sec=10, SR=0.25, Perm=5.0x10 ⁻⁶	
	mole/(cm ² -sec -atm),H ₂ /CO=100, CO ₂ /CO=1	17
Figure 7	Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed	
	reactors. (Conditions same as in Figure 6)	18
Figure 8	Hydrogen Recovery (%) in catalytic Membrane Reactor (conditions same as in	
	Figure 6)	18
Figure 9	Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in	
	membrane along the Membrane Side (conditions same as in Figure 6)	19
Figure 10	CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors.	
	T(C)=275, Por(atm)=7.8027, Pom(atm)=1, ST sec=10, SR=0.25, Perm=10x10 ⁻⁶	
	mole/(cm ² -sec -atm),H ₂ /CO=100, CO ₂ /CO=1	20
Figure 11	Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed	
	reactors. (Conditions same as in Figure 10)	21
Figure 12	Hydrogen Recovery (%) in catalytic Membrane Reactor (conditions same as in	
	Figure 10)	22
Figure 13	Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in	
	membrane along the Membrane Side (conditions same as in Figure 10)	23
Figure 14	CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors.	
	T(C)=275, Por(atm)=7.8027, Pom(atm)=1, ST sec=10, SR=0.25, Perm=5x10 ⁻⁶	
	mole/(cm ² -sec -atm),H ₂ /CO=1000, CO ₂ /CO=10	24
Figure 15	Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed	
	reactors. (Conditions same as in Figure 14)	25

Figure 16	Hydrogen Recovery (%) in catalytic Membrane Reactor (conditions same as in	
	Figure 14)	26
Figure 17	Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in	
	membrane along the Membrane Side (conditions same as in Figure 14)	27
Figure 18	CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors.	
	T(C)=275, Por(atm)=7.8027, Pom(atm)=1, ST sec=10, SR=0.25, Perm=5x10 ⁻⁶	
	mole/(cm ² -sec -atm),H ₂ /CO=100, CO ₂ /CO=2	28
Figure 19	Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed	
	reactors. (Conditions same as in Figure 18)	29
Figure 20	Hydrogen Recovery (%) in catalytic Membrane Reactor (conditions same as in	
	Figure 18)	30
Figure 21	Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in	
	membrane along the Membrane Side (conditions same as in Figure 18)	31
Figure 22	CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors.	
	T(C)=275, Por(atm)=7.8027, Pom(atm)=1, ST sec=10, SR=0.25, Perm=5x10 ⁻⁶	
	mole/(cm ² -sec -atm),H ₂ /CO=100, CO ₂ /CO=10	32
Figure 23	Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed	
	reactors. (Conditions same as in Figure 22)	33
Figure 24	Hydrogen Recovery (%) in catalytic Membrane Reactor (conditions same as in	
	Figure 22)	34
Figure 25	Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in	
	membrane along the Membrane Side (conditions same as in Figure 22)	35
Figure 26	CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors.	
	T(C)=275, Por(atm)=7.8027, Pom(atm)=1, ST sec=10, SR=0.25, Perm=5x10 ⁻⁶	
	mole/(cm ² -sec -atm),H ₂ /CO=100, CO ₂ /CO=100	36
Figure 27	Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed	
	reactors. (Conditions same as in Figure 26)	37
Figure 28	Hydrogen Recovery (%) in catalytic Membrane Reactor (conditions same as in	
	Figure 26)	38
Figure 29	Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in	
	membrane along the Membrane Side (conditions same as in Figure 26)	38

1. INTRODUCTION

Upon the recommendation of the review panel, we began preliminary investigation on the use of the hydrotakite materials we developed as CO_2 adsorbents in parallel to our on-going membrane synthesis development. One of the major thrusts of our hydrotakite materials is their reversible adsorption of CO_2 at the intermediate temperature (200 to 300°C) and in the presence of steam, which are uniquely suitable for the low temperature shift (LTS)of the water gas shift (WGS) reaction. While the membrane synthesis activity is in progress, we began the investigation on the use of the hydrotakite as an adsorbent. In this report we summarize our findings on the potential opportunities of the use of the hydrotakite adsorbent for separation of CO_2 for sequestration. Since our project targets the improvement of WGS efficiency with concomitant CO_2 removal for sequestration, we limit our discussion here on the process schemes which can improve the WGS efficiency via the removal of CO_2 using adsorptive process. Also, the membrane suggested for the proposed scheme is the carbon molecular sieve membrane suitable for H2 and CO2 removal available from us.

2. EXECUTIVE SUMMARY

Upon the recommendation of the review panel, we began to investigate the use of the hydrotalcite material we developed as an adsorbent, in parallel to our hydrotalcite membrane synthesis activities. Two process schemes have been identified for the use of this hydrotalcite as an adsorbent: Adsorption Enhanced WGS Pack-bed reactor and Adsorption Enhanced WGS membrane (H₂ Selective) Reactor. In this quarter, we focus on the simulation of the 2^{nd} scheme, Adsorption Enhanced WGS Membrane Reactor. Depending upon the permeance of and the selectivity of the membrane, 5% to 30% conversion enhancement over the conventional WGS pack-bed reactor are obtained with the proposed adsorption enhanced membrane reactor. The membrane selectivity of CO₂/CO also plays an important role. For a highly hydrogen selective membrane (i.e., with minimum or no permeation of CO₂), 5% conversion enhancement was obtained. However, when CO_2/CO selectivity increases to 100, the enhancement was increased to 30%. A newly complete conversion of CO was obtained since cycle time is dependent upon the hydrotalcite adsorption isotherm, an optimization study may be required to determine an optimum selectivity for a given hydrotalcite capacity. Optimization will be performed in the next quarterly report in addition to the simulation of the 1st case: Adsorption Enhanced WGS packed-bed.

3. EXPERIMENTAL

3.1 Process Alternatives for Using Hydrotalcite as Adsorbents

Two process schemes have been identified to meet the criteria of improving the WGS

efficiency with the concomitant removal of CO_2 for sequestration. They are Case I: Adsorption Enhanced WGS Packed Bed Reactor, and Case II: Adsorption Enhanced WGS Membrane Reactor. They are presented in the next page along with Base Case: WGS Packed Bed Reactor in conjunction with CO₂ removal via HT through pressure swing adsorption (PSA). In Base Case, the hydrotalcite adsorber is used as a 2^{nd} stage separator for the removal of CO₂ for sequestration. As a conventional adsorber, it does not involve in the WGS reaction. Case I involves the use of the hydrotalcite adsorbent mixed with the WGS catalyst in a packed bed; thus, the reaction product CO_2 can be removed in-situ to enhance the WGS reaction. Since the adsorbent is used in the process, multiple beds with switching bed operation are required: One to a minimum two beds are required for adsorption while the other for regeneration. Case II integrates a hydrogen and CO₂ selective membrane which is (used as a WGS membrane reactor) packed with hydrotalcite for CO₂ removal in the permeate side. Thus, both reaction products, i.e., hydrogen and CO₂, can be removed via the membrane. In addition to the removal of CO₂, the hydrotalcite adsorption in the permeate side can enhance the CO_2 permeance in order to produce a high purity hydrogen product stream efficiently. Again, the use of adsorbent mandates switching bed type operation as in Case I. Case IIA is also proposed as a modifier of Case II. Instead of using a hybrid single stage reactor, Case IIA employs an interstage hydrotalcite adsorbent as a separator. Although the process scheme requires an additional stage, the adsorber can be operated independent of the WGS reactor. While the CO₂ selective hydrotalcite membrane is presently under development, our carbon molecular hydrogen selective membrane has demonstrated its efficacy for this purpose. They can be tailored with a highly hydrogen selectivity (i.e., H2/CO2>10) or a balanced selectivity with $KH_2/CO_2 < 10$. For Case II a compromised membrane is recommended, while for Case IIA a highly hydrogen selective membrane is preferred. For this project, we recommend the simulation of both Case I and II for comparison with Base Case. The simulation will offer the preferred performance of the hydrotalcite adsorbent and its operating condition for each case. Further its operating economic analysis will be performed for defining the performance requirement of the hydrotalcite adsorbent.

3.2 Literature Review on Adsorption- and Membrane – Enhanced Reactor

Reactive separation processes have been attracting renewed interest for application in catalytic steam reforming and other reactions. They include packed-bed catalytic membrane reactors [Saracco and Specchia, 1994; Sanchez and Tsotsis, 2002], and more recently adsorptive reactor processes [Han and Harrison, 1994; Ortiz and Harrison, 2001]. Their potential **a**lvantages, over the more conventional reformers, have been widely discussed. They include: (i) increasing reactant conversion and product yield, to overcome the thermodynamic limitation of conversion. This, potentially, allows one to operate under milder conditions (e.g., lower temperature and pressures, and reduced steam consumption); (ii) reducing the downstream purification requirements by *in situ* separating from the reaction mixture the desired product

Process Alternatives using Hydrotalcites as Adsorbents For CO₂ Separation/Sequestration Applications:

Base Case: Conventional WGS and HT Adsorber



Case I: Adsorption Enhanced WGS Reactor



Case II: Adsorption Enhanced WGS Membrane Reactor



<u>Case IIA</u>: WGS Membrane Reactor with Interstage CO₂ Adsorber



hydrogen (in the case of membrane reactors), or the undesired product CO_2 (in the case of adsorptive reactors).

Membrane reactors show substantial promise in this area and, typically, utilize nanoporous non-metallic inorganic or dense metallic Pd or Pd-alloy membranes [Sanchez and Tsotsis, 2002]. The latter are better suited for pure hydrogen production. However, metallic membranes are very expensive, and become brittle during reactor operation or deactivate in the presence of sulfur or coke. Nanoporous nao-metallic inorganic membranes are better suited for reactive environments discussed. They are generally difficult to manufacture, however, without cracks and pin-holes, and as a result product purity is inferior to that of the metallic membrane. In addition, the hydrogen product in the permeate side contains substantial amounts of other by-products, due to its less-than-perfect separation. In this project we propose the development of the hydrotalcite membrane taking the advantage of the high selectivity of the dense membrane made with non-metallic materials CO_2^{W} while this membrane is presently under development, we will utilize the carbon molecular sieve membrane we have developed for this purpose.

Adsorptive reactors also show good potential [Ortiz and Harrison, 2001]. The challenge here, however, is in matching the adsorbent properties with those of the catalytic system. Tw of adsorbents have been suggested. Potassium-promoted layer double hydroxides (I H_2 which operate stably only at temperatures ~ 400-450 °C [Ding and Alpay, 2000a,b], and CaO or commercial dolomite, which can be utilized at the typical steam reforming temperatures of 650 – 700 °C, but requires temperatures higher than 850 °C for regeneration [Ortiz and Harrison, 2001]. The latter are very harsh conditions, and result in gradual deterioration of the adsorbent properties, and potentially sintering of the catalysts [Ortiz and Harrison, 2001]. The mismatch between the reaction and regeneration conditions is, likely, to result, furthermore, in significant process complications. In the project, we will use the layer double hydroxide as in the former case, but with working capacity in the temperature range suitable for LTS-WGS.

Our proposed Case II, termed the Hybrid Adsorbent-Membrane Reactor (HAMR) system was recently proposed by our subcontractor, USC [Park and Tsotsis, 2004], which couples the reaction and membrane separation steps with adsorption on the reactor and/or membrane permeate side. The HAMR system investigated previously involved a hybrid pervaporation membrane reactor system, and integrated the reaction and pervaporation step through a membrane with water adsorption. Coupling reaction, pervaporation and adsorption significantly improved performance. In this report we investigate a HAMR system involving a hybrid-type packed-bed catalytic membrane reactor coupling the water gas shift reaction through a porous carbon membrane with a CO_2 adsorption system. This HAMR system shows behavior, which is more advantageous than either the membrane or the conventional reactors in

terms of the attained yields and selectivities. In addition, the HAMR system allows potentially for significantly greater process flexibility than either the membrane or the adsorptive reactor system. The membrane, for example, can be used to separate the catalyst from the adsorbent phases, thus allowing for *in situ* continuous regeneration of the adsorbent. This offers a significant advantage over the adsorptive reactors, which are, by definition, discontinuous systems, and require the presence of multiple beds (one being in operation, while the other is being regenerated) to simulate continuous operation. The HAMR system shows, furthermore, significant potential advantages with respect to the conventional membrane reactor (MR) system. Beyond the improved yields and selectivities, the HAMR system has the potential for producing a fuel-cell grade hydrogen product without CO_2 , which is of significance for the hydrogen production from coal gasification.

4. Results and Discussion

In this quarterly report, a mathematical model for Case II, i.e., HAMR system, is presented and analyzed, for a range of temperature and pressure conditions. The behavior of the HAMR system is compared with Base Case, i.e., conventional packed-bed reactor. In the next quarter, we will present Case I. The feed into the WGS HAMR reactor is the exit stream from a conventional steam reformer.

THEORY

Kinetics for water gas shift reaction

For the water gas shift reaction we utilize a catalytic reaction rate first proposed by Ovesen *et al.* [1996] as follows:

$$CO + H_2O \leftrightarrows CO_2 + 3H_2 \tag{1}$$

$$r = A \exp\left(-\frac{86500}{RT}\right) \frac{P_{CO}P_{H_{2}O}^{1.4}}{P_{CO_{2}}^{0.7}P_{H_{2}}^{0.9}} \frac{1}{P_{t}^{0.4}}(1-\boldsymbol{b})$$
(2)

$$\boldsymbol{b} = \frac{1}{Ke} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$$
(3)

$$Ke = \exp\left(\frac{4577.8}{T} - 4.33\right)$$

The mathematical model of the HAMR system

A schematic of the HAMR system is shown in Fig. 1. In this figure the catalyst is packed in the interior of the membrane (signified by the superscript F, for feed-side), while the adsorbent is packed in the exterior membrane volume (signified by the superscript P, or

permeate-side). There are, of course, a number of other potential reactor configurations. For example, the adsorbent and catalyst can be loaded together in the internal membrane space, while the adsorbent may also be loaded in the external membrane space. Or the catalyst and adsorbent may only be loaded in the internal membrane space. To simplify matters, in the development of the model, we will assume that external mass transfer resistances are negligible for the transport through the membrane, as well as for the reaction steps, and that internal diffusion limitations for the catalyst, and internal or external transport limitations for the adsorbent are accounted for by overall rate coefficients. Also plug-flow conditions are assumed to prevail for both the interior and exterior membrane volumes, as well as ideal gas law conditions



Fig. 1 Schematic diagram of a packed bed membrane reactor

The HAMR system is assumed, furthermore, to operate under quasi-steady conditions with reaction/transport processes in the catalyst and transport properties through the membrane relaxing much faster than the slow changes in the adsorbent state due to saturation.

We assume further that the reactor utilizes a porous, inactive carbon molecular sieve

membrane, and that transport through the membrane is Fickian. We recognize that such assumption is, likely, not valid for CMS membranes. The transport phenomena through such membranes still remain a topic of ongoing research [Sahimi and Tsotsis, 2003] by our group and others, and properly describing their transport characteristics remains a challenge, which goes beyond the narrow scope of this preliminary report. In this report mass transfer through the porous membrane is described through the following equation:

$$F_j = U_j (P_j^F - P_j^P) \tag{4}$$

where F_j is the molar flux (mol/m².s), P_j^F partial pressure of component j on the membrane

feed-side (bar), P_i^P partial pressure of component j on the membrane permeate-side (bar), and

 U_j the membrane permeance for component *j* (mol/m².bar.s). To simplify calculations in this preliminary "proof of concept" phase we will assume that U_j depends only on the membrane properties, like the thickness and the pore characteristics of the membrane layer. For CMS membranes U_j , in addition, depends both on the upstream and downstream pressures. For the reactor calculations in this report, however, it will be taken to be pressure independent. In future reports, more elaborate relationships describing the pressure dependence of permeance will be utilized.

The mass balance on the feed-side of the reactor packed with WGS catalyst and, potentially, with an adsorbent is described by the following equations for CO, H_2 , H_2O , and an inert species (potentially used as a sweep gas or a blanketing agent -- for the WGS reaction a practical sweep gas would be either steam or hydrogen, however):

$$\frac{dn_j^F}{dV} = -\boldsymbol{a}_m \boldsymbol{U}_j (\boldsymbol{P}_j^F - \boldsymbol{P}_j^P) + (1 - \boldsymbol{e}^F) \boldsymbol{b}_c \, \boldsymbol{r}_c \boldsymbol{R}_j^F$$
(5)

where n_j^F is the molar flow rate for species $j \pmod{s}$, V the feed-side reactor volume variable (m³), \boldsymbol{a}_m the membrane area per feed-side reactor volume (m²/m³), \boldsymbol{e}^F the feed-side bed porosity, \boldsymbol{b}_c the fraction of the solid volume occupied by catalysts ($\boldsymbol{b}_c = 1$, when no adsorbent is present – then, Eqn. 5 is also valid for CO₂), \boldsymbol{r}_c the catalyst density (Kg/m³), and R_j^F the reaction rate expression, which is either described by Eqn. 1 above (mol/Kg.s), or is equal to zero if j is an inert species.

For CO_2 , when adsorbent is present, the following equation applies:

$$\frac{dn_{CO_2}^F}{dV} = -\boldsymbol{a}_m U_{CO_2} (P_{CO_2}^F - P_{CO_2}^P) + (1 - \boldsymbol{e}^F) \boldsymbol{b}_c \boldsymbol{r}_c R_{CO_2}^F - (1 - \boldsymbol{e}^F) (1 - \boldsymbol{b}_c) \boldsymbol{r}_a G_{CO_2}^F$$
(6)

where \mathbf{r}_a is the adsorbent density (Kg/m³), and $G_{CO_2}^F$ is the rate of CO₂ adsorption

(mol/Kg.s). One finds a number of approaches in the literature for describing $G_{CO_2}^F$. Ideally, one would like to account explicitly for both external and internal mass transport, and finite rates of adsorption. Such an approach goes beyond the scope of this preliminary report, however, in addition to the fact that there are currently no experimental high temperature transport/adsorption CO₂ data to justify this level of mathematical technical detail. Traditionally, in the modeling of adsorptive reactors simpler models have been utilized, instead [Ding and Alpay, 2000a,b]. Two such models have received the most attention. They are: (i) the model based on the assumption of instantaneous local adsorption equilibrium (ILE) between the gas and the adsorbent phases [Ding and Alpay, 2000a,b; Park and Tsotsis, 2004], and the linear driving force models (LDF), according to which [Karger and Ruthven, 1992]

 $G_{CO_2}^F$ is described by the following expression:

$$G_{CO_2}^F = k_a (C_{seq} - C_s)$$
⁽⁷⁾

where C_{seq} is the adsorption equilibrium CO₂ concentration on the adsorbent (mol/Kg), C_s is the existing adsorbed CO₂ concentration (mol/Kg), and k_a (s⁻¹) is a parameter which "lumps" together the effects of external and intraparticle mass transport and the sorption processes, and which, as a result, is often a strong function of temperature and pressure [Ding and Alpay, 2000a,b] – though, typically, in modeling is taken as temperature/pressure independent. For calculating C_{eq}^s , for CO₂ adsorption on a potassium promoted hydrotalcite (LDH) Ding and Alpay [2000a,b] have shown that this adsorbent follows a Langmuir adsorption isotherm both under dry and wet conditions, described by the following equation.

$$C_{seq} = \frac{m_{CO_2} b_{CO_2} P_{CO_2}}{1 + b_{CO_2} P_{CO_2}}$$
(8)

where m_{CO_2} (mol/Kg) is the total adsorbent capacity, and b_{CO_2} (bar⁻¹) the adsorption equilibrium constant is described the van't Hoff equation

$$b_{CO_2} = b_{CO_2}(T_0) \exp(-\Delta H_a / R(1/T - 1/T_0))$$
(9)

The heat of adsorption ΔH_a under wet conditions for a region of temperatures from 481 -753 K was calculated to be -17 kJ/mol, while b_{CO_2} at 673 K is equal to 23.6 bar [Ding and Alpay, 2000a,b].

Eqns. 5 and 6 are complemented by the initial conditions

$$V = 0; n_j^F = n_{j0}^F = \left(F_0^F x_{j0}^F P_0^F\right) / RT$$
(10)

where F_0^F is the volumetric flow rate at the inlet of the reactor feed-side (m³/s), x_{j0}^F the inlet mole fraction for species j, and P_0^F the inlet total pressure on the feed-side (bar).

Assuming that the catalyst particles and adsorbent particles have the same size, pressure drop in a packed bed can be calculated using Ergun equation:

$$-\frac{dP^{F}}{dZ} = 10 \times 10^{-7} \frac{f^{F} \left(G^{F}\right)^{2}}{g_{c} d_{P}^{F} \boldsymbol{r}_{F}^{F}}$$
(11a)

$$f^{F} = \left(\frac{1-\boldsymbol{e}^{F}}{\boldsymbol{e}^{F}}\right) \left(1.75 + \frac{150(1-\boldsymbol{e}^{F})\boldsymbol{m}^{F}}{N_{\text{Re}}^{F}}\right)$$
(11b)

$$N_{\rm Re}^F < 500(1 - e^F)$$
 (11c)

$$N_{\rm Re}^F = \frac{d_P^F G^F}{\mathbf{m}^F}$$
(11d)

where P^F is the pressure in feed side (bar), \mathbf{m}^F the viscosity in feed side (poise), d_P^F the particle diameter in feed side (cm), G^F the superficial mass velocity in feed side (gr/(cm².sec), Z the reactor length (cm), and \mathbf{r}_F^F the fluid density in feed side (gr/cm³)

By dividing both sides of the Ergun equation by the cross-sectional area (A^F) of the reactor feed side, we can express the pressure drop per unit volume of the reactor as:

$$-\frac{dP^{F}}{dV} = 10 \times 10^{-7} \frac{f^{F} \left(G^{F}\right)^{2}}{A^{F} g_{c} d_{P}^{F} \boldsymbol{r}_{F}^{F}}$$
(12a)

at V=0,
$$P^F = P_0^F$$
 (12b)

For the permeate side the equations for CO, H₂, H₂O, and the inert (if utilized) are as follows:

$$\frac{dn_j^P}{dV} = \boldsymbol{a}_m U_j (P_j^F - P_j^P)$$
(13)

For CO₂ on the permeate-side, when adsorbent is present

$$\frac{dn_{CO_2}^{P}}{dV} = \boldsymbol{a}_m U_{CO_2} (P_{CO_2}^{F} - P_{CO_2}^{P}) - (1 - \boldsymbol{e}^{P}) \boldsymbol{gr}_a G_{CO_2}^{P}$$
(14)

where e^{P} is the permeate-side bed porosity (when $e^{P}=1$ no adsorbent is present and 14 reduces to Eqn. 13) and g the ratio of the cross-sectional area on the permeate-side to cross-sectional area on the feed-side.

Eqns. 13 and 14 are complemented by the initial conditions

$$V = 0; n_j^P = n_{j0}^P = \left(F_0^P x_{j0}^P P_0^P\right) / RT$$
(15)

where F_0^P is the volumetric flow rate at the inlet of the reactor permeate-side (m³/s), x_{j0}^P the inlet mole fraction for species j on the permeate side, and P_0^P the inlet total pressure on the permeate-side (bar).

Pressure drop in the permeate side, again can be calculated by Ergun equation:

$$-\frac{dP^{P}}{dV} = 10 \times 10^{-7} \frac{f^{P} (G^{P})^{2}}{A^{P} g_{c} d_{P}^{P} \boldsymbol{r}_{F}^{P}}$$
(16a)

at V=0,
$$P^P = P_0^P$$
 (16b)

in which

$$f^{P} = \left(\frac{1-\boldsymbol{e}^{P}}{\boldsymbol{e}^{P}}\right) \left(1.75 + \frac{150(1-\boldsymbol{e}^{P})\boldsymbol{m}^{P}}{N_{\text{Re}}^{P}}\right)$$
(16c)

$$N_{\rm Re}^{P} < 500(1 - e^{P}) \tag{16d}$$

$$N_{\rm Re}^{P} = \frac{d_{P}^{P}G^{P}}{\boldsymbol{m}^{P}}$$
(16e)

The reactor conversion (based on CO, typically the limiting reagent) is defined by the following Eqn.:

$$X_{CO} = \frac{n_{CO0}^{F} - \left(n_{CO,ex}^{F} + n_{CO,ex}^{P}\right)}{n_{CO_{4}0}^{F}}$$
(17)

where $n_{CO_4,ex}^F$ and $n_{CO_4,ex}^P$ are the CO molar flow rates at the exit of the reactor feed- and permeate-sides correspondingly (mol/s).

The product hydrogen yield is defined by the following Eqn.:

$$Y_{H_2} = \frac{n_{H_2,ex}^F + n_{H_2,ex}^P}{n_{CO0}^F}$$
(18)

where $n_{H_2,ex}^F$ and $n_{H_2,ex}^P$ are the hydrogen molar flow rates at the exit of the reactor feed- and permeate-sides correspondingly (mol/s). In the HAMR simulations we also calculate the hydrogen recovery ratio which is defined as the fraction of product hydrogen that is recovered in the membrane permeate side and the amount of CO impurity (in ppm) that the permeate hydrogen stream contains.

RESULTS AND DISCUSSION

For all simulations presented here the basic assumption is that the WGS HAMR and the conventional packed bed reactor follow as a second stage an isothermal steam reformer which operates under the following conditions:

P=100 psig

T=750 °C

 $CH_4:H_2O:H_2 = 13:0.1$

The exit from the steam reformer is assumed to be at equilibrium and is used intact (without any water make-up) as the feed to the WGS reactors. The conditions in the WGS reactors are as follows:

T=275°C

P=100psig

The membrane is hydrogen selective and the ideal separation factors (ratios of individual permeances) are assumed as follows:

(H₂/CO₂)=(H₂/CO)=(H₂/H₂O)=(H₂/CH₄)=100:1

We have first investigated the effect of permeance. Figs 2-5 are for the case where the hydrogen permeance is equal to 1×10^{-6} mole/(cm².sec.atm).

Fig. 2 CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors. T(C)=275,P0r(atm)=7.8027,P0m(atm)=1,ST sec=10,SR=0.25xe=0.93637





Fig. 3 Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed reactors.



Fig. 5 Permeate CO Concentration in Catalytic Membrane Reactor.



For Figs. 69 the hydrogen permeance was taken equal to $5.x10^{-6}$ mole/(cm².sec.atm).





T(C)=275,P0r(atm)=7.8027,P0m(atm)=1,ST sec=10,SR=0.25xe=0.93637



Fig. 7 Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed reactors.

Fig. 8 Hydrogen Recovery (%) in catalytic Membrane Reactor.





Fig. 9 Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in membrane along the Membrane Side

The next four figures are for a hydrogen permeance of 10×10^{-6} mole/(cm².sec.atm).



Fig. 10 CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors.



Fig. 11 Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed



Fig. 12 CO Conversionvs. Reactor length for catalytic membrane vs. packed bed



It is obvious from Figs. 2-13 that the HAMR system clearly outperforms the conventional WGS reactor. The membrane permeance has a very significant effect on reactor performance. Very desirable hydrogen recoveries and CO contaminant levels are attained for the higher permeances. In terms of the overall performance the above results point out that there is an optimal value of permeance that provides a good performance in terms of yield, hydrogen recovery without unduly impacting the CO contaminant levels in the hydrogen product. It should be noted that the above values of permeances and separation factors are currently being attained with our carbon molecular sieve membranes.

It should be noted that the CO contaminant levels in the hydrogen product can be further reduced by improving the membrane CO separation characteristics. The following Figures are from a simulation run with a hydrogen membrane permeance of $5.x \ 10^{-6}$ mole/(cm².sec.atm) and the following separation characteristics

 $(H_2/CO_2)=(H_2/H_2O)=(H_2/CH_4)=100:1$



Fig. 14 CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors. T(C)=275, P0r(atm)=7.8027, P0m(atm)=1, ST sec=10, SR=0.25xe=0.93637



Fig. 15 Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed reactors. T(C)=275,P0r(atm)=7.8027,P0m(atm)=1,ST sec=10,SR=0.25xe=0.93637



Fig. 16 Hydrogen Recovery (%) in catalytic Membrane Reactor.



Fig. 17 Permeate CO Concentration in Catalytic Membrane Reactor.

For the next set of runs we have investigated the effect of the membrane's separation characteristics. The other conditions remain the same and the permeance was taken equal to $5.x10^{-6}$ mole/(cm².sec.atm). For the next four Figs. the membrane was assumed to exhibit the following separation factors:

 $(H_2/CO)=(H_2/H_2O)=(H_2/CH_4)=100:1$

(H₂/CO₂)=50:1



Fig. 18 CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors. $\label{eq:transform} {}^{T(C)=275,P0r(atm)=7.8027,P0m(atm)=1,ST \ sec=10,SR=0.25xe=0.93637}$



Fig. 19 Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed reactors. T(C)=275,P0r(atm)=7.8027,P0m(atm)=1,ST sec=10,SR=0.25xe=0.93637





Fig. 21 Permeate CO Concentration in Catalytic Membrane Reactor.

For the next four Figs. the membrane was assumed to exhibit the following separation

factors:

(H₂/CO)=(H₂/H₂O)=(H₂/CH₄)=100:1 (H₂/CO₂)=10:1



Fig. 22 CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors. T(C)=275,P0r(atm)=7.8027,P0m(atm)=1,ST sec=10,SR=0.25xe=0.93637



Fig. 23 Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed





Fig. 25 Permeate CO Concentration in Catalytic Membrane Reactor.

For the next four Figs. the membrane was assumed to exhibit the following separation

factors:

H₂/CO)=(H₂/H₂O)=(H₂/CH₄)=100:1

(H₂/CO₂)=1:1



Fig. 26 CO Conversion vs. Reactor length for catalytic membrane vs. packed bed reactors. T(C)=275,P0r(atm)=7.8027,P0m(atm)=1,ST sec=10,SR=0.25xe=0.93637



Fig. 27 Unconverted CO vs. Reactor length for catalytic membrane vs. packed bed



Fig. 29 Permeate CO Concentration in Catalytic Membrane Reactor. CO PPM in membrane along the Membrane Side



From Figs. 18-29 above one notes that the separation characteristics have a significant effect on reactor performance. As the CO_2H_2 permeance ratio decreases hydrogen yield, recovery and purity all improve.

CONCLUSIONS

We have investigated a novel reactor system, termed the Hybrid Adsorbent-Membrane Reactor (HAMR), for hydrogen production through the water gas shift reaction. The HAMR combines the reaction and membrane separation steps with adsorption on the membrane permeate-sides using the hydrotalcite material we developed under this project. This HAMR system is of potential interest to pure hydrogen production for hydrogen production from coal gasification off-gas. The reactor performance has been investigated for a range of membrane characteristics and compared with the behavior of the traditional packedbed reactor. The HAMR outperforms the conventional reactor system. It shows enhanced CO conversion, hydrogen yield, and product purity, and provides good promise for meeting the product purity requirements for PEM operation.

BIBLIOGRAPH

- Y. Ding, and E. Alpay, Adsorption-enhanced steam-methane reforming, *Chem. Eng. Sci.*, 55, 3929, 2000a.
- Y. Ding, and E. Alpay, Equilibria and kinetics of CO₂ adsoprtion on hydrotalcite adsorbent, Chem. Eng. Sci., 55, 346, 2000b.
- C. Han, and D.P. Harrison, Simultaneous shift reaction and carbon dioxide separation for the direct production of hydrogen, *Chem. Eng. Sci.*, **49**, 5875, 1994.
- J. Karger, and D.M. Ruthven, Diffusion in zeolites and other microporous solids, New York: Wiley, 1992.
- A.L.Ortiz, and D.P. Harrison, Hydrogen production using sorption-enhanced reaction, *Ind. Eng. Chem. Res.*, 40, 5102, 2002.
- B.G. Park, and T.T. Tsotsis, A Novel pervaporation membrane reactor integrated with a water adsorbent system for equilibrium reactions," *Chem. Eng. Processing*, in press.
- M. Sahimi, and T.T. Tsotsis, Molecular pore network models of nanoporous materials," *Physica B*, 338, 291, 2003.
- G. Saracco, and V. Specchia, Catalytic inorganic-membrane reactors: present experience and future opportunities, *Catal. Rev. -Sci. Eng.*, **36**, 305, 1994.