HYBRID ADSORPTIVE MEMBRANE REACTOR

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ABSTRACT

A hybrid adsorbent-membrane reactor in which the chemical reaction, membrane separation, and product adsorption are coupled. Also disclosed are a dual-reactor apparatus and a process using the reactor or the apparatus.

40 Claims, 56 Drawing Sheets
FIG. 1
\[ T(C)=275, P_{Or} (\text{atm})=7.8027, P_{Om} (\text{atm})=1, ST \ sec=10, SR=0.25x=e=0.93637 \]
FIG. 3

Unconverted CO in catalytic membrane reactor
--- Unconverted CO in Plug flow reactor

\[ T(C) = 275, P(\text{atm}) = 7.8027, P_0(\text{atm}) = 1, \text{ST sec} = 10, \text{SR} = 0.25, e = 0.93637 \]
FIG. 7

Uncertained CO in catalyst membrane reactor

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Uncertained CO in Plug flow reactor
FIG. 8

Hydrogen Recovery Percent

Hydrogen Recovery

Dimensionless length
图 10

CO 转化率在催化膜反应器和 Plug flow 反应器中的比较。
FIG. 13

CO ppm in membrane along the membrane side

Dimensionless length

CO Mpp

10^{-3} 10^{-2} 10^{-1} 10^{0}
FIG. 14

CO conversion in catalytic membrane reactor

CO conversion in plug flow reactor
FIG. 19

Unconverted CO in catalytic membrane reactor

Unconverted CO in Plug flow reactor

\[ T(C) = 275, P_{O_2}(atm) = 7.8027, P_{O_2}(atm) = 1, ST \text{ sec} = 10, SR = 0.25, e = 0.93637 \]
FIG. 21

CO PPM in membrane along the Membrane Side

Dimensionless length

10^3 10^2 10^1 10^0

1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

1 0 0 0 0 0 0 0 0 0
FIG. 24

Hydrogen Recovery Percent

Dimensionless length
Hydrogen Product, >99% with <1 ppm CO

Reject containing CH₄, CO₂, residual H₂ and trace CO as fuel for boiler

Optional Downstream Hydrogen Enrichment Loop

The stream compositions are presented here as an example generated from mathematical simulation using parameters obtained from existing catalysts, adsorbents, and membranes. Two reformers are required for PSA operation if a continuous hydrogen stream is required.

- Catalysts, e.g., Ni-based or emerging ones
- CO₂-adsorbent, e.g., hydrotalcite

Hydrogen Production via Steam Reforming with Membrane- and Adsorption-Enhanced Reactor at Low Temperature (350 to 400°C)

Figure 30
Figure 31

Figure 32a

Permeance and Selectivity vs. Temperature
CMS Membrane ID: DZ-143856
Permeance vs. Temperature
Membrane ID: CMS - 136099

![Graph showing permeance vs. temperature for different gases (Hydrogen, Helium, Nitrogen). The x-axis represents temperature in °C, and the y-axis represents permeance in m³/m²·mbar. The graph includes lines for each gas, indicating their permeance values at various temperatures.]

Figure 32b
Figure 33

Hydrothermal Stability
Membrane ID: CMS - 149834; Temp = 220°C

Permeance, dry [m³/hr/bar]

- 20 psig. steam
- 50 psig. steam

- Hydrogen
- Helium
- Nitrogen

Time [hours]

Figure 34

Effect of Hexane Vapor on He Permeance
CMS Membrane ID: DZ-109142

- 180°C
- 150°C
- 80°C

Permeance [m³/hr]

Time [hr]
FIG. 35
FIG. 39

HAMR - W/n = 50
HAMR - W/n = 100
HAMR - W/n = 200
HAMR - W/n = 300

Recovery

Dimensionless Time

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

1

10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
FIG. 50

intercept = ln(ko) = 25.90
slope = \(E = -114.218.6\)
\(r^2 = 0.986402922\)
Figure 56a Prior Art

**Base Case:** Conventional WGS and HT Adsorber

Base Case Diagram:
- Coal
- Gasifier
- Off-gas
- WGS Packed Bed
- CO₂
- CO₂ to Sequestration
- CO₂ Ad/Desorption - HT-PSA
- H₂

Figure 56b

**Case II:** Adsorption Enhanced WGS Reactor

Case II Diagram:
- Gasifier
- Off-gas
- WGS - Packed Bed
- CO₂ Ad/Desorption - HT/PSA
- H₂
- CO₂
Figure 57a

**Case II:** Adsorption Enhanced WGS Membrane Reactor

**Figure 57b**

**Case IIa:** WGS Membrane Reactor with Interstage CO₂ Adsorber
HYBRID ADSORPTIVE MEMBRANE REACTOR

RELATED APPLICATION

This application claims priority to U.S. Provisional Application Ser. No. 60/653,035, filed Feb. 14, 2005, the content of which is incorporated herein by reference in its entirety.

FUNDING

This invention was made with support in part by grants from the United States National Aeronautics and Space Administration (NASA) and Department of Energy (DOE) under cooperative agreement No. DE-FC26-00NT40922. Therefore, the U.S. government has certain rights.

FIELD OF THE INVENTION

The present invention relates generally to chemical reactors. More specifically, the invention relates to a hybrid adsorbent-membrane reactor (HAMR) and uses thereof.

BACKGROUND OF THE INVENTION

As a result of stricter environmental regulations worldwide, hydrogen is progressively becoming a very important clean energy source for both mobile and stationary applications. For hydrogen to replace fossil fuels as the fuel of choice for mobile applications, it requires the creation of a production and delivery infrastructure equivalent to that currently exist for fossil fuels. As an alternative and an interim step toward the new hydrogen economy, various groups are currently investigating hydrocarbon steam reforming for onboard generation of hydrogen for use in fuel cell-powered vehicles, or for on-site production, in place of compressed or liquid hydrogen gas storage for stationary power generation vehicles, or for on-site production, in place of compressed or liquid hydrogen gas storage for stationary power generation (Choi and Stenger (2003) J. Power Sources 124:432, Darwish et al. (2003) Fuel 83:409, Liu et al. (2002) J. Power Sources 111:83, and Semelsberger et al. (2004) Int. J. Hydrogen Energy 29:1047). The process is widely practiced for large-scale hydrogen production and involves reacting steam with methane, through the endothermic and reversible steam reforming reaction, over supported nickel catalyst in packed bed reactors (reformers). Traditionally, these reformers have generally operated at temperatures often in excess of 1,000 K and pressures as high as 30 bar and reach relatively low equilibrium conversions (Elnashaie et al. (1990) Chem. Eng. Sci. 45:491, Xu and Froment (1989) AIChE J. 35:88, and Han and Harrison (1994) Chem. Eng. Sci. 49:5875). Such conditions are often neither convenient nor economical to attain for small-scale, on-site (or onboard) hydrogen generation. As a result, there is much current interest in the development of more effective reforming technologies.


MRs show substantial promise in this area and, typically, utilize nanoporous inorganic or metallic Pd or Pd alloy membranes (Sanchez and Tsotsis (2002) Catalytic Membranes and Membrane Reactors, Wiley-VCH, Weinheim, Germany). The latter are better suited for pure hydrogen production. However, metallic membranes are very expensive and become brittle during reactor operation (Nam et al. (2000) Korean J. Chem. Eng. 17:288) or deactivate in the presence of sulfur or coke. Nanoporous membranes are better suited for the steam reforming environment. They are difficult to manufacture, however, without cracks and pinholes and, as a result, often have inferior product yield. In addition, the hydrogen product in the permeate side contains substantial amounts of other byproducts, particularly CO2, and may require further treatment for use in fuel cell-powered vehicles.


Conventional steam reforming, particularly for methane (CH4), has been studied extensively and practiced routinely in the industry using a packed bed catalytic reactor (PBR). A high reaction temperature is required (i.e., >800°C for CH4) to deliver a sufficient reaction rate and to overcome the equilibrium conversion limitations; this introduces an unfavorable environment for the exothermic water-gas-shift (WGSR) reaction step. As a result, significant CO is present in the final product, which requires further conversion to H2 in a separate
two-stage WGS reactor and additional post-treatment reactors (such as a partial oxidizer and a methanizer) to reduce the CO levels to meet the proton exchange membrane (PEM) feedstock specifications. This multiple-step reforming process adds significant process complexity, and is undesirable, particularly for small-scale distributed-type applications. MR technology (Sanchez Marcano and Tsotsis (2002) Catalytic Membranes and Membrane Reactors, Wiley VCH), primarily Pd membrane-based, has been proposed to streamline the reforming process by, for instance, integrating the reforming and WGS reaction in a single step or via the use of a one-step WGS. However, this Pd membrane-based MR suffers the following disadvantages: potential coking on the Pd surface as a result of H2 removal even at the lowest operating temperature, e.g., >450°C; and only incremental, not dramatic increases in overall conversion resulting from bulk H2 removal. Theoretically, a nearly 100% conversion can be achieved by completely removing the H2 from the reactor side; however, the partial pressure of H2 available for permeation is too low for this to be realized in practice.

In the case of natural gas (NG), the reforming reaction is typically modeled as reforming of methane (by far its major component), which consists of the following two reactions:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2; \Delta H = +206.2 \text{ kJ/mol} \quad (1') \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2; \Delta H = -41.2 \text{ kJ/mol} \quad (2')
\end{align*}
\]

Reaction (1') is endothermic and equilibrium limited, and is, therefore, practiced at higher temperatures (>800°C). Unfortunately, the WGS reaction (2') is exothermic and is highly unfavorable at higher temperatures. This then necessitates the need for utilizing a separate reactor system for carrying out the WGS step at lower temperatures. The WGS reactor system is typically a dual-reactor system consisting of a high temperature reactor operating at 800-900°C, followed by a low temperature reactor, which operates at ~250-300°C. This, then, adds significant process complexity to the fuel processing section. Nevertheless, even with the separate WGS reactor being present, the product contains ~0.5-1% CO, substantially higher than what is permissible, for example, for PEM fuels cells. To make the use of such fuel cells possible (CO at the tens of ppm level is detrimental to performance for power generation and mobile applications), an additional processing step for CO removal, typically a partial oxidation step (POX), is required, which further adds to the processing complexity and costs.

**SUMMARY OF THE INVENTION**

The invention is based upon the unexpected discovery that a novel hybrid adsorbent-membrane reactor requires less hostile operating conditions and provides enhanced product yield and purity.

Accordingly, in one aspect, the invention features a reactor comprising a chamber, an inlet for introducing one or more reactants into the chamber, a catalyst disposed in the chamber for facilitating a reaction of the reactants to produce at least one desired product and at least one by-product, a non-metallic membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane, an adsorbent disposed in the chamber for adsorbing the by-product, and an outlet for allowing the desired product to exit the chamber.

In another aspect, the invention features a reactor comprising a chamber, an inlet for introducing one or more reactants into the chamber, a catalyst disposed in the chamber for facilitating a steam reforming reaction of the reactants to produce at least one desired product and at least one by-product, a non-metallic membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane, an adsorbent disposed in the chamber for adsorbing the by-product, and an outlet for allowing the desired product to exit the chamber.

The invention further provides a reactor comprising a chamber, an inlet for introducing one or more reactants into the chamber, a catalyst disposed in the chamber for facilitating a steam reforming reaction of the reactants to produce at least one desired product and at least one by-product, a membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane, a hydrotalcite (HT) adsorbent disposed in the chamber for adsorbing the by-product, and an outlet for allowing the desired product to exit the chamber.

The invention also provides a reactor comprising a chamber, an inlet for introducing one or more reactants into the chamber, a catalyst disposed in the chamber for facilitating a steam reforming reaction of the reactants to produce at least one desired product and at least one by-product, a membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane, an adsorbent disposed in the chamber for adsorbing the by-product, and an outlet for allowing the desired product to exit the chamber.

Moreover, the invention provides a reactor comprising a chamber, an inlet for introducing one or more reactants into the chamber, a catalyst disposed in the chamber for facilitating a reaction of the reactants to produce at least one desired product and at least one by-product, a membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane, and a hydrotalcite adsorbent disposed in the chamber for adsorbing the by-product, and an outlet for allowing the desired product to exit the chamber.

Also within the scope of the invention is a process comprising introducing one or more reactants into a reactor of the invention, contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product, selectively passing the desired product and the by-product through the membrane, adsorbing the by-product with the adsorbent, and withdrawing the desired product from the reactor.

In some embodiments, the invention provides an apparatus comprising at least two reactors of the invention.
reforming reaction of the reactants to produce at least one desired product and at least one by-product, a membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane, an adsorbent disposed in the chamber for adsorbing the by-product, and an outlet for allowing the desired product to exit the chamber.

Accordingly, the invention provides a process comprising introducing one or more reactants into each reactor of an apparatus of the invention, contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product in the reactor, selectively passing the desired product and the by-product through the membrane in the reactor, adsorbing the by-product with the adsorbent in the reactor, and withdrawing the desired product through the membrane in the reactor, adsorbing the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product in the reactor, wherein the reactors of the apparatus are offset in point of time such that, at all times, the desired product is being withdrawn from at least one of the reactors.

In a reactor of the invention, the reaction may be a WGS or steam reforming reaction, the membrane may be a CMS or silicon carbide membrane, and the adsorbent may be a hydrotalcite. A process of the invention may be carried out at 275-700° C.

The above-mentioned and other features of this invention and the manner of obtaining and using them will become more apparent, and will be best understood, by reference to the following description, taken in conjunction with the accompanying drawings. These drawings depict only typical embodiments of the invention and do not therefore limit its scope.

**BRIEF DESCRIPTION OF THE FIGURES**

**FIG. 1** is a schematic diagram of an HAMR.

**FIG. 2** shows CO conversion vs. reactor length for HAMR vs. packed bed reactors. T=275° C., P_r=7.8027 atm, P_m=1 atm, Space Time (ST)=10 sec, Sweep Ratio (SR)=0.25, Equilibrium Conversion (Xe)=0.93637.

**FIG. 3** shows unconverted CO vs. reactor length for HAMR vs. packed bed reactors. (Conditions same as in FIG. 2)

**FIG. 4** shows hydrogen recovery (%) in HAMR. (Conditions same as in FIG. 2)

**FIG. 5** shows permeate CO concentration (in ppm) in HAMR. (Conditions same as in FIG. 2)

**FIG. 6** shows CO conversion vs. reactor length for HAMR vs. packed bed reactors. T=275° C., P_r=7.8027 atm, P_m=1 atm, ST=10 sec, SR=0.25, Xe=0.93637, H_2 permeance=5x 10^{-6} mole/(cm^2 sec atm), H_2/CO=100, CO_2/CO=1.

**FIG. 7** shows unconverted CO vs. reactor length for HAMR vs. packed bed reactors. (Conditions same as in FIG. 6)

**FIG. 8** shows hydrogen recovery (%) in HAMR. (Conditions same as in FIG. 6)

**FIG. 9** shows permeate CO concentration (in ppm) in HAMR. (Conditions same as in FIG. 6)

**FIG. 10** shows CO conversion vs. reactor length for HAMR vs. packed bed reactors. T=275° C., P_r=7.8027 atm, P_m=1 atm, ST=10 sec, SR=0.25, Xe=0.93637, H_2 permeance=10x 10^{-6} mole/(cm^2 sec atm), H_2/CO=100, CO_2/CO=1.

**FIG. 11** shows unconverted CO vs. reactor length for HAMR vs. packed bed reactors. (Conditions same as in FIG. 10)

**FIG. 12** shows hydrogen recovery (%) in HAMR. (Conditions same as in FIG. 10)

**FIG. 13** shows permeate CO concentration (in ppm) in HAMR. (Conditions same as in FIG. 10)

**FIG. 14** shows CO conversion vs. reactor length for HAMR vs. packed bed reactors. T=275° C., P_r=7.8027 atm, P_m=1 atm, ST=10 sec, SR=0.25, Xe=0.93637, H_2 permeance=5x 10^{-6} mole/(cm^2 sec atm), H_2/CO=100, CO_2/CO=10.

**FIG. 15** shows unconverted CO vs. reactor length for HAMR vs. packed bed reactors. (Conditions same as in FIG. 14)

**FIG. 16** shows hydrogen recovery (%) in HAMR. (Conditions same as in FIG. 14)

**FIG. 17** shows permeate CO concentration (in ppm) in HAMR. (Conditions same as in FIG. 14)

**FIG. 18** shows CO conversion vs. reactor length for HAMR vs. packed bed reactors. T=275° C., P_r=7.8027 atm, P_m=1 atm, ST=10 sec, SR=0.25, Xe=0.93637, H_2 permeance=5x 10^{-6} mole/(cm^2 sec atm), H_2/CO=100, CO_2/CO=10.

**FIG. 19** shows unconverted CO vs. reactor length for HAMR vs. packed bed reactors. (Conditions same as in FIG. 18)

**FIG. 20** shows hydrogen recovery (%) in HAMR. (Conditions same as in FIG. 18)

**FIG. 21** shows permeate CO concentration (in ppm) in HAMR. (Conditions same as in FIG. 18)

**FIG. 22** shows CO conversion vs. reactor length for HAMR vs. packed bed reactors. T=275° C., P_r=7.8027 atm, P_m=1 atm, ST=10 sec, SR=0.25, Xe=0.93637, H_2 permeance=5x 10^{-6} mole/(cm^2 sec atm), H_2/CO=100, CO_2/CO=10.

**FIG. 23** shows unconverted CO vs. reactor length for HAMR vs. packed bed reactors. (Conditions same as in FIG. 22)

**FIG. 24** shows hydrogen recovery (%) in HAMR. (Conditions same as in FIG. 22)

**FIG. 25** shows permeate CO concentration (in ppm) in HAMR. (Conditions same as in FIG. 22)

**FIG. 26** shows CO conversion vs. reactor length for HAMR vs. packed bed reactors. T=275° C., P_r=7.8027 atm, P_m=1 atm, ST=10 sec, SR=0.25, Xe=0.93637, H_2 permeance=5x 10^{-6} mole/(cm^2 sec atm), H_2/CO=100, CO_2/CO=100.

**FIG. 27** shows unconverted CO vs. reactor length for HAMR vs. packed bed reactors. (Conditions same as in FIG. 26)

**FIG. 28** shows hydrogen recovery (%) in HAMR. (Conditions same as in FIG. 26)

**FIG. 29** shows permeate CO concentration (in ppm) in HAMR. (Conditions same as in FIG. 26)

**FIG. 30** is a schematic diagram showing hydrogen production via steam reforming with membrane- and adsorption-enhanced reactor at low temperature (350-400° C.).

**FIG. 31** shows a Media and Process Technology, Inc. (M&P) CMS membrane.

**FIG. 32a** shows temperature dependence of the permeance and selectivity of an M&P CMS membrane (targeting 50 to 250° C. applications).

**FIG. 32b** shows temperature dependence of the permeance of an M&P CMS membrane.

**FIG. 33** shows hydrothermal stability of a CMS membrane.

**FIG. 34** shows resistance to poisoning of CMS membranes.

**FIG. 35** is a schematic diagram of a HAMR system.

**FIG. 36** shows H_2 yield for HAMR and AR systems for different W_/d_{CH_4,0}.

**FIG. 37** shows CO_2 concentration (wet basis) profiles at the reactor outlet for AR and HAMR systems at different W_/d_{CH_4,0}.

**FIG. 38** shows H_2 yield for HAMR and AR systems for different W_/d_{CH_4,0}.
FIG. 38 shows CO concentration (wet basis, in ppm) profiles in the HAMR permeate side exit and AR exit for different W/F. FIG. 39 shows hydrogen recovery for an HAMR system at different W/F. FIG. 40 shows effect of βc on hydrogen yield for HAMR and AR systems. FIG. 41 shows effect of βc on CO exit concentration (wet basis, in ppm) for HAMR (permeate) and AR systems. FIG. 42 shows effect of Λ on hydrogen yield. FIG. 43 shows effect of Ω on hydrogen yield. FIG. 44 shows effect of Ω on hydrogen recovery. FIG. 45 shows effect of sweep ratio on hydrogen yield. FIG. 46 shows hydrogen yield at 400°C. FIG. 47 shows time-averaged CO concentration (wet basis, in ppm) at 400°C for HAMR and AR systems. FIG. 48 shows CO2 isotherms and Langmuir fitting. FIG. 49 shows an experimental set-up. FIG. 50 is an activation energy plot. FIG. 51 shows CO conversion vs time (W/F=300). FIG. 52 shows CO2 exit flow rate vs time (W/F=330). FIG. 53 shows CO conversion vs time (W/F=350). FIG. 54 shows CO2 exit flow rate vs time (W/F=350). FIG. 55 shows CH4 conversion vs time. FIG. 56a shows conventional WGS and HT Adsorber. FIG. 56b shows Adsorption Enhanced WGS Reactor. FIG. 57a shows Adsorption Enhanced WGS Membrane Reactor. FIG. 57b shows WGS Membrane Reactor with Interstage CO2 Adsorber.

DETAILED DESCRIPTION OF THE INVENTION

A new HAMR system involving a hybrid packed bed catalytic membrane reactor coupling the methane steam reforming reaction through a porous ceramic membrane with a CO2 adsorption system was investigated. The present HAMR system is of potential interest to pure hydrogen production for PEM fuel cells for various mobile and stationary applications. The reactor characteristics were investigated for a range of temperature and pressure conditions relevant to the aforementioned applications. The HAMR system exhibited enhanced methane conversion, hydrogen yield, and product purity and showed good promise for reducing the hostile operating conditions of conventional methane steam reformers and for meeting the product purity requirements for PEM operation.

In another study, the use of hydrotalcite as an adsorbent was investigated in an adsorption-enhanced WGS methane (H2 selective) reactor. One of the major thrusts of hydrotalcite is its reversible adsorption of CO2 at intermediate temperature (200 to 300°C) and in the presence of steam, which are uniquely suitable for the low temperature shift (LTS) of the WGS reaction. Depending upon the permeance and selectivity of the membrane, 5% to 30% conversion enhancement over conventional WGS packed bed reactor was obtained. The membrane selectivity of CO2/CO also played 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 CO2/CO selectivity increased to 100, the enhancement was increased to 30%.

Accordingly, the invention provides various hybrid adsorptive membrane reactors and related apparatus. The basic components of a reactor include: (a) a chamber, (b) an inlet for introducing one or more reactants into the chamber, (c) a catalyst disposed in the chamber for facilitating a reaction of the reactants to produce at least one desired product and at least one by-product, (d) a membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane, (e) an adsorbent disposed in the chamber for adsorbing the by-product, and (f) an outlet for allowing the desired product to exit the chamber. Conventional membrane reactors are well-known in the art. See, e.g., “Hydrogen Production from Methane Steam Reforming Assisted by Use of Membrane Reactor,” Natural Gas Conversion, pp 509-515, Elsevier Science Publishers B.V., Amsterdam (1991). In contrast to the conventional membrane reactors, a reactor of the invention couples the chemical reaction and membrane separation with product adsorption. This reactor can be used for equilibrium- or selectivity-limited reactions such as esterification, WGS, steam reforming, and various dehydrogenation, dehydration, and condensation reactions. The reactants can be either liquids or gases, e.g., steam and methane, natural gas, or naphtha.

For example, the most common industrial process for the production of hydrogen involves steam reforming and WGS reactions. Steam reforming is the reaction between methane or naphtha (e.g., heptane) and steam to produce H2 (desired product) and CO (by-product). WGS is the reaction between CO and steam to produce H2 (desired product) and CO2 (by-product).

Any of the commonly used catalysts can be employed in a reactor of the invention. Examples of catalysts for steam reforming and WGS reactions include nickel-alumina, nickel-magnesium alumina, and the noble metal catalysts.

A membrane of the invention preferably has high permeation rates and permeselectivities towards reaction products. Examples of membranes for steam reforming and WGS reactions include CMS, silicon carbide, Pt and its alloys, aluminum nitride, and various dense, and other nanoporous membranes. In some embodiments, the product (desired product or by-product) permeance of such an membrane may be in the range of 1.153e-7 to 1.153e-5 mole/(cm² sec atm), the permeselectivity of desired product/reactant may be in the range of 10-200, and the permeselectivity of desired product/by-product may be in the range of 10-200.

In some embodiments, the membrane may be attached to a supporting substrate as a top layer. The supporting substrate (e.g., a ceramic support) is mechanically strong, is stable under reaction conditions, and shows high permeation rates such that it does not limit the membrane throughput.

An adsorbent of the invention is used to sorb a by-product either by physical or chemical sorption and release the sorbed by-product under reduced partial pressure of the by-product. The adsorbent should be effectively non-catalytic and otherwise inert as to reactants and products as well as to any purge or pressurizing gases so as to avoid any significant occurrence of side reactions. An exemplary adsorbent for carbon dioxide is a hydrotalcite such as AlO(OH)2Mg(OH)2·2H2O or other desiccants such as CaO, various commercial dolomites, drierite, and various other desiccant compounds.

In some embodiments, the catalyst is disposed in the feed side of the membrane, while the adsorbent is disposed in the permeate side of the membrane. The feed side of the membrane is where the reactants are fed and the permeate side of the membrane is the other side. In this case, a membrane highly selective for the product is preferred. For example, the permeselectivity of product/reactant may be larger than 50.

In other embodiments, a mixture of the adsorbent and the catalyst is disposed in the feed side of the membrane.

In still other embodiments, while a mixture of the adsorbent and the catalyst is disposed in the feed side of the mem-
branes, an additional amount of the adsorbent is disposed in the permeate side of the membrane. In yet other embodiments, the adsorbent is disposed in a separate compartment away from the catalyst and the membrane. See, for example, Case IIA in Example I below.

In some embodiments, the catalyst and adsorbent are preferably in granular form or pelletized so that they can be readily mixed and not tend to stratify during the operation. Such granules can be suspended in a porous matrix or in a free form. Other methods of securing the catalyst and adsorbent in fixed beds can be employed, provided they do not impede access of the reactants and products to the surfaces of these materials.

A process of the invention generally includes the steps of (a) introducing one or more reactants into a reactor of the invention, (b) contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product, (c) selectively passing the desired product and the by-product through the membrane, (d) adsorbing the by-product with the adsorbent, and (e) withdrawing the desired product from the reactor.

Preferably, a process of the invention is carried out at 75-750°C, e.g., 75-95, 110-175, 150-200, 200-300, 250-325, 350-500, 500-650, or 650-750°C. In some embodiments, the pressure of the reactants is in the range of 0-2,500 psig, e.g., 0-20, 20-100, 100-250, 250-500, 500-1,000, or 1,000-2,500 psig upon entering into the reactor.

The preferred molar ratio of reactants upon entering into a reactor may vary according to the type of the reaction. For example, for a steam-methane reforming reaction, the molar ratio of H₂O:CH₄ upon entering into a reactor is preferably in the range of 2-5. For a steam-naphtha (heptane) reforming reaction, the molar ratio of H₂O:CH₃₄ is preferably in the range of 7-14. For a WGS reaction, the molar ratio of H₂O:CO can be preferably in the range of 1-4.

In some embodiments, an apparatus of the invention contains at least two reactors of the invention. In operation of such an apparatus, each reactor is used as described above, and the reactors are offset in point of time such that, at all times, a desired product is being withdrawn from at least one of the reactors.

As used herein, a range of X-Y includes X, Y, and any number between X and Y. The following examples are intended to illustrate, but not to limit, the scope of the invention. While such examples are typical of those that might be used, other procedures known to those skilled in the art may alternatively be utilized. Indeed, those of ordinary skill in the art can readily envision and produce further embodiments, based on the teachings herein, without undue experimentation.

Example I

CO₂ Selective Ceramic Membrane for Water-Gas-Shift Reaction with Concomitant Recovery of CO₂

Two process schemes were investigated for the use of hydrotalcites as CO₂ adsorbents to enhance WGS reaction: Case I (FIG. 56b) involved the adsorption-enhanced WGS packed bed reactor (AR) and Case II (FIG. 57a) involved the adsorption-enhanced WGS membrane reactor (HAMR). They are presented here along with Base Case (FIG. 56a) (WGS Packed Bed Reactor in conjunction with CO₂ removal via pressure swing adsorption (PSA)). Both cases were to improve the WGS reactor efficiency via the concomitant removal of CO₂ for sequestration. The AR system has been discussed in the literature (see, e.g., Waldron et al. (2001) AIChE J. 47:1477 and Huflon et al. (1999) AIChE J. 45:248).

The HAMR system included 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 were investigated for a range of permeance and selectivity relevant to the aforementioned application. The HAMR system showed enhanced CO conversion, hydrogen yield, and product purity, and provided good promise for reducing the hostile operating conditions of conventional WGS reactors, and for meeting the CO₂ sequestration objective.

In Base Case, the hydrotalcite adsorber was used as a 2nd stage separator for the removal of CO₂ for sequestration. As a conventional adsorber, it did not involve in the WGS reaction. Case I involved the use of the hydrotalcite adsorbent mixed with the WGS catalyst in a packed bed; thus, the reaction product CO₂ could be removed in situ to enhance the WGS reaction. Since the adsorbent was used in the process, multiple beds with switching bed operation were usually required to reach a steady state production of hydrogen. Case II integrated a hydrogen and CO₂ selective membrane (used as a WGS membrane reactor) which was packed with hydrotalcite for CO₂ removal in the permeate side. Thus, both reaction products, i.e., hydrogen and CO₂, could be removed via the membrane. In addition to the removal of CO₂, the hydrotalcite adsorption in the permeate side could enhance the CO₂ permeance in order to produce a high purity hydrogen product stream efficiently. Again, the use of adsorbent mandated switching bed type operation as in Case I. Case IIA (FIG. 57b) was also proposed as a modifier of Case II. Instead of using a hybrid single stage reactor, Case IIA employed an interstage hydrotalcite adsorbent as a separator. Although the process scheme required an additional stage, the adsorbent could be operated independently of the WGS reactor.

The carbon molecular hydrogen selective membrane (available from M&P) demonstrated its efficacy for this purpose. Such membrane can be tailored with a high hydrogen selectivity (i.e., K(H₂/CO₂)≥10) or a balanced selectivity with K(H₂/CO₂)<10. For Case II, a compromised membrane is recommended, while for Case IIA, a highly hydrogen selective membrane is preferred. Other alternative membranes can be considered here. For instance, a CO₂ selective hydrotalcite membrane has the advantage of a high selectivity of the dense membrane made with non-metallic materials. Hydrotalcite, a well-known CO₂ affinity adsorbent, was used in the simulation as an example.

The simulation of both Case I and II for comparison with Base Case would offer the preferred performance of the hydrotalcite adsorbent and its operating condition for each case. Further, its operating economic analysis would define the performance requirement of the hydrotalcite adsorbent.

A HAMR system involving a hybrid-type packed bed catalytic membrane reactor coupling the WGS reaction through a porous carbon membrane with a CO₂ adsorption system was investigated. This HAMR system showed behavior more advantageous than either the membrane or the conventional reactors in terms of the attained yields and selectivities. In addition, the HAMR system allowed potentially for significantly greater process flexibility than either the membrane or the adsorptive reactor system. The membrane, for example, could be used to separate the catalyst from the adsorbent phases, thus allowing for in situ continuous regeneration of the adsorbent. This would offer a significant advantage over the adsorptive reactors which are, by definition, discontinu-
ous systems and require the presence of multiple beds (one being in operation while the other being regenerated) to simulate continuous operation. The HAMR system showed, furthermore, significant potential advantages with respect to the conventional MR system. Beyond the improved yields and selectivities, the HAMR system had the potential for producing a fuel cell grade hydrogen product without CO2, which is of significance for the hydrogen production from coal gasification.

Theory
A mathematical model for Case II, i.e., HAMR system, is presented and analyzed, for a range of temperature and pressure conditions without any intention to be bound by such theory. The behavior of the HAMR system is compared with Base Case, i.e., conventional packed bed reactor. The feed into the WGS HAMR reactor is the exit stream from a conventional steam reformer.

Kinetics for WGS Reaction
For the WGS reaction, a catalytic reaction rate first proposed by Ovesen et al. (1996) J. Catal. 158:170 is utilized as presented and analyzed, for a range of temperature and pressure conditions: 

\[ \frac{d n}{d V} = -\alpha U_j (P_j^F - P_j^P) + (1 - \epsilon)^e \beta_j \rho_j \epsilon_R \]

where \( \eta_j^F \) is the molar flow rate for species \( j \) (mol/s), \( V \) the feed-side reactor volume variable (m⁴), \( \alpha_m \) the membrane area per feed side reactor volume (m²/m³), \( \beta \) the fraction of the solid volume occupied by catalysts (\( \beta = 1 \) when no adsorbent is present—then, Eqn. 5 is also valid for \( CO_2 \)), \( \rho_j \) 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:

\[ \frac{dn_{CO_2}}{dV} = -\alpha_{U}(n_{CO_2}) (P_{CO_2}^F - P_{CO_2}^P) + (1 - \epsilon) \beta \rho_{CO_2} \]

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, for 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, it is assumed 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. 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.

It is assumed further that the reactor utilizes a porous, inactive CMS membrane, and that transport through the membrane is Fickian. Here, mass transfer through the porous membrane is described through the following equation:

\[ F_j = \frac{U_j (P_j^F - P_j^P)}{R_j^F} \]

where \( F_j \) is the molar flux (mol/m²s), \( P_j^F \) partial pressure of component \( j \) on the membrane feed-side (bar), \( P_j^P \) 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, it is assumed 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 here, however, it is taken to be pressure-independent.

The mass balance on the feed side of the reactor packed with WGS catalyst and, potentially, with an adsorbent is described by the following equation 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):

\[ \frac{dn_j}{dV} = -\alpha_{U_j} (P_j^F - P_j^P) + (1 - \epsilon)^e \beta_j \rho_j \epsilon_R \]

where \( \eta_j^F \) is the molar flow rate for species \( j \) (mol/s), \( V \) the feed-side reactor volume variable (m⁴), \( \alpha_m \) the membrane area per feed side reactor volume (m²/m³), \( \beta \) the fraction of the solid volume occupied by catalysts (\( \beta = 1 \) when no adsorbent is present—then, Eqn. 5 is also valid for \( CO_2 \)), \( \rho_j \) 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:

\[ \frac{dn_{CO_2}}{dV} = -\alpha_{U} (n_{CO_2}) (P_{CO_2}^F - P_{CO_2}^P) + (1 - \epsilon) \beta \rho_{CO_2} \]

where \( \rho_j \) is the adsorbent density (Kg/m³), and \( G_{CO_2} \) is the rate of \( CO_2 \) adsorption (mol/Kg/s). One finds a number of approaches in the literature for describing \( G_{CO_2} \). Ideally, both external and internal mass transport as well as finite rates of adsorption would be explicitly accounted for. Traditionally, in the modeling of adsorptive reactors, simpler models have been utilized, instead (Ding and Alpay (2000) Chem. Eng. Sci. 55:3929 and Ding and Alpay (2000) Chem. Eng. Sci. 55:346). 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 (2000) Chem. Eng. Sci. 55:3929, Ding and Alpay (2000) Chem. Eng. Sci. 55:346, and Park and Tsotsis (2004) System. Chem. Eng. Proc. 43:1171), and the linear driving force models (LDF), according to which (Karger and Ruthven (1992) Diffusion in zeolites and other microporous solids, New York, Wiley), \( G_{CO_2} \) is described by the following expression:

\[ G_{CO_2} = -k_s(C_{eq} - C_j) \]

where \( C_{eq} \) is the adsorption equilibrium \( CO_2 \) concentration on the adsorbent (mol/Kg), \( C_j \) is the existing adsorbed \( CO_2 \) concentration (mol/Kg), and \( k_s \) is a parameter which "jumps" 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 (2000) Chem. Eng. Sci. 55:3929 and Ding and Alpay (2000) Chem. Eng. Sci. 55:346)—although, typically, in modeling, is taken as temperature/pressure-independent. For
calculating \( C_{CO_2} \), for \( CO_2 \) adsorption on a potassium-promoted hydrotalcite (LDH), it has been shown (Ding and Alpay 2000) Chem. Eng. Sci. 55:3929 and Ding and Alpay (2000) Chem. Eng. Sci. 55:346) that this adsorbent follows a Langmuir adsorption isotherm both under dry and wet conditions, described by the following equation:

\[
C_{CO_2} = \frac{m_{CO_2} b_{CO_2} P_{CO_2}}{1 + b_{CO_2} P_{CO_2}}
\]

(8)

where \( m_{CO_2} \) (mol/Kg) is the total adsorbent capacity, and \( b_{CO_2} \) (bar\(^{-1}\)) is the adsorption equilibrium constant described in the van’t Hoff equation:

\[
b_{CO_2} = b_{CO_2}(T_o) \exp\left(-\frac{\Delta H_a}{RT_o}\right)
\]

(9)

where the heat of adsorption \( \Delta H_a \) under wet conditions for a region of temperatures from 481-753 K is calculated to be \(-17 \pm \text{kJ/mol} \), while \( b_{CO_2} \) at 673 K is equal to 23.6 bar (Ding and Alpay (2000) Chem. Eng. Sci. 55:3929 and Ding and Alpay (2000) Chem. Eng. Sci. 55:346).

For \( CO_2 \) on the permeate side, when adsorbent is present,

\[
d\bar{P}_{CO_2} \frac{dV}{dV} = a_{CO_2} U_f (P_{CO_2} - P_f)
\]

(14)

where \( \epsilon_f \) is the permeate side bed porosity (when \( \epsilon_f = 1 \) no adsorbent is present and 14 reduces to Eqn. 13) and \( y \) the ratio of the cross-sectional area on the permeate side to cross-sectional area on the feed side.

Eqs. 13 and 14 are complemented by the initial conditions:

\[
V=0; \quad \bar{P}^{P} = \frac{1}{2}(P_{CO_2}^{P} - P_{CO_2}^{F})RT
\]

(15)

where \( F_0^P \) is the volumetric flow rate at the inlet of the reactor permeate-side (m\(^3\)/s), \( x_{j0}^P \) the inlet mole fraction for species \( j \), and \( P_{CO_2}^{P} \) the inlet total pressure on the permeate side (bar).

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

\[
\frac{dP}{dV} = 10 \times 10^{-4} \frac{f^P (G_f^P)^2}{A^P \mu F}
\]

(16a)

at \( V=0, \quad \bar{P}^P = P_{CO_2}^{P} \)

in which

\[
f^P = \frac{1}{3.75} + \frac{150(1 - \epsilon_f) \mu_f}{N_f}
\]

(16b)

\[N_f < 500(1 - \epsilon_f)\]

(16c)

\[N_f = \frac{d_f^P G_f^P}{\mu_f}\]

(16d)

The reactor conversion (based on \( CO_2 \), typically the limiting reagent) is defined by the following equation:

\[
X_{CO_2} = \frac{n_{CO_2}^{exit} + n_{CO_2}^{PP}}{n_{CO_2}^{F}}
\]

(17)

where \( n_{CO_2}^{exit} \) and \( n_{CO_2}^{PP} \) are the \( CO_2 \) 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 equation:

\[
\eta_{H_2} = \frac{n_{H_2}^{exit} + n_{H_2}^{PP}}{n_{CO_2}^{F}}
\]

(18)

where \( n_{H_2}^{exit} \) and \( n_{H_2}^{exit} \) are the hydrogen molar flow rates at the exit of the reactor feed- and permeate-sides correspondingly (mol/s). In the HAMR simulations, the hydrogen recovery ratio is also calculated. The hydrogen recovery ratio 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.

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

\[ P = 100 \text{ psig} \]
\[ T = 750^\circ \text{C} \]
\[ \text{CH}_4:\text{H}_2\text{O}:\text{H}_2 = 1:3:0.1 \]

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

\[ T = 275^\circ \text{C} \]
\[ P = 100 \text{ psig} \]

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

\[ (\text{H}_2/\text{CO}_2): (\text{H}_2/\text{CO}) : (\text{H}_2/\text{H}_2\text{O}) : (\text{H}_2/\text{CH}_4) = 100:1 \]

The effect of permeance was first investigated. FIGS. 2-5 are for the case where the hydrogen permeance was equal to \(1 \times 10^{-6} \text{ mole/(cm}^2\text{•sec•atm)}\). For FIGS. 6-9, the hydrogen permeance was taken equal to \(5 \times 10^{-6} \text{ mole/(cm}^2\text{•sec•atm)}\). FIGS. 10-13 are for a hydrogen permeance of \(10 \times 10^{-6} \text{ mole/(cm}^2\text{•sec•atm)}\).

It is obvious from FIGS. 2-13 that the HAMR system clearly outperformed the conventional WGS reactor. The membrane permeance had a very significant effect on reactor performance. Very desirable hydrogen recoveries and CO contaminant levels were 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 and 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 were attained with CMS membranes available from M&P.

It should be noted that the CO contaminant levels in the hydrogen product can be further reduced by improving the membrane CO separation characteristics. FIGS. 14-17 are from a simulation run with a hydrogen membrane permeance of \(5 \times 10^{-6} \text{ mole/(cm}^2\text{•sec•atm)}\) and the following separation characteristics:

\[ (\text{H}_2/\text{CO}_2): (\text{H}_2/\text{CO}) : (\text{H}_2/\text{H}_2\text{O}) : (\text{H}_2/\text{CH}_4) = 100:1 \]

\[ (\text{H}_2/\text{CO}) = 1:000:1 \]

For the next set of runs, the effect of the membrane’s separation characteristics was investigated. The other conditions remained the same and the permeance was taken equal to \(5 \times 10^{-6} \text{ mole/(cm}^2\text{•sec•atm)}\). For FIGS. 18-21, the membrane was assumed to exhibit the following separation factors:

\[ (\text{H}_2/\text{CO}) = (\text{H}_2/\text{H}_2\text{O}) : (\text{H}_2/\text{CH}_4) = 100:1 \]
\[ (\text{H}_2/\text{CO}) = 50:1 \]

For FIGS. 22-25, the membrane was assumed to exhibit the following separation factors:

\[ (\text{H}_2/\text{CO}) = (\text{H}_2/\text{H}_2\text{O}) : (\text{H}_2/\text{CH}_4) = 10:1 \]
\[ (\text{H}_2/\text{CO}) = 1:1 \]

For FIGS. 26-29, the membrane was assumed to exhibit the following separation factors:

\[ (\text{H}_2/\text{CO}) = (\text{H}_2/\text{H}_2\text{O}) : (\text{H}_2/\text{CH}_4) = 100:1 \]
\[ (\text{H}_2/\text{CO}) = 1:1 \]

From FIGS. 18-29, it is noted that the separation characteristics had a significant effect on reactor performance. As the CO/\(\text{H}_2\) permeance ratio decreased, hydrogen yield, recovery, and purity all improved.

The HAMR combines the reaction and membrane separation steps with adsorption on the membrane permeate sides using the hydrotalcite material. This HAMR system is of potential interest to pure hydrogen production for hydrogen production from coal gasification off-gas. The reactor performance was investigated for a range of membrane characteristics and compared with the behavior of the traditional packed bed reactor. The HAMR outperformed the conventional reactor system. It showed enhanced CO conversion, hydrogen yield, and product purity, and provided good promise for meeting the product purity requirements for PEM operation.

Example II

A High Efficiency, Low Temperature Reformer for Hydrogen Production

Description of the Technology

The technology involves the use of a high-efficiency, low-temperature reactor for steam reforming. With this reactor system, \(\text{H}_2\) production can be operated at 350 to 400° C., as opposed to >800° C. The essence of the process is the employment of a unique membrane- and adsorption-enhanced reformer, which can preferentially allow \(\text{H}_2\) permeation and CO adsorption simultaneously, the two ultimate reaction products from steam reforming. Thus, the reformer can produce a \(\text{H}_2\) product continuously until the adsorbent is saturated for regeneration via PSA. This unique reactor configuration can be viewed as a simplified MR under PSA operation, suitable for a scaled-down version of the steam reforming process. MR technology and sorption-enhanced PSA proposed in the literature allow only one of the reaction products, such as \(\text{H}_2\) or \(\text{CO}_2\), to be removed; the reaction rate enhancement that results is not sufficient, however, to achieve significant reforming at such low temperatures.

The membrane utilized is a CMS nanoporous membrane originally developed by USC and currently offered commercially by M&P for lab and field-testing. Its unique \(\text{H}_2\) permselectivity at the proposed temperature is ideal for this application. As noted above, Pd membranes are also known for their unique \(\text{H}_2\) permselectivity; however, several barriers related to material stability remain to be overcome. Moreover, their viable operating temperature range is incompatible with the proposed temperature range for reactor operation. The adsorbent selected is a hydrotalcite-based adsorbent, which has been intensively studied (Yang et al. (2002) Chem. Eng. Sci. 57:2945 and Kim et al. (2004) Ind. Eng. Chem. Res. 43:4559); its \(\text{CO}_2\) affinity at this operating condition has also been well-documented in the literature (see Yang et al. (2002) Chem. Eng. Sci. 57:2945 for additional references). A mathematical model has been developed and a numerical simulation has been performed to support the technical feasibility of the process. FIG. 30 shows a schematic of the process together with the results of process design calculations using this model. Combining the adsorbent with the reforming catalyst in a packed bed MR utilizing the CMS membranes results in hydrocarbon conversion four times higher than the thermodynamic equilibrium conversion level; thus, efficient reforming can be accomplished at this low temperature range. The reformed product is low in \(\text{CO}\) (e.g., <10 ppm), and is, therefore, ready as a feedstock for fuel cell applications. The product, if desired, can be further enriched by processing it in a downstream \(\text{H}_2\) separator (see process scheme in FIG. 30).

The Advantages

Existing processes for hydrogen production are (i) extremely energy-intensive due to the requirement of steam (as a reactant) supply at this high temperature, and the need for providing the energy for the endothermic reforming reac-
HARLEM is also fuel-flexible. Using the mathematical model, its application to the case of liquid hydrocarbon fuels such as naphtha has been simulated. According to Darwish et al. (2004) Fuel 83:409, naphtha can be represented as C\textsubscript{m}H\textsubscript{n}, where m=7.3 and n=15.5. In the simulations presented here, naphtha is represented as a heptane molecule; other authors in their reactor simulations of naphtha reforming (Chen et al. (2003) AIChE J. 49:1250, Chen et al. (2003) Ind. Eng. Chem. Res. 42:6549, and Chen et al. (2004) Ind. Eng. Chem. Res. 43:1323) have also used heptane as a model compound to represent naphtha. For such a fuel, in addition to reactions (1') and (2') above, the following reaction also takes place:

\[
\text{C}_{7}\text{H}_{16} + 7\text{H}_{2} \rightarrow \text{CO} + 15\text{H}_{2} \text{O} + 1108 \text{kJ/mol} \quad (\text{3})
\]

The reforming temperature for liquid hydrocarbons is lower, i.e., \(\sim 600^\circ\text{C}\), and no thermodynamic equilibrium conversion limitation exists in this temperature range according to the literature (Darwish et al. (2004) Fuel 83:409). Unfortunately, the methanation reaction (the reverse of the reforming reaction (1')) above) becomes significant and results in the formation of CH\textsubscript{4} in addition to significant unconverted CO. In the proposed dual-enhanced process, the removal of H\textsubscript{2} as a product in conjunction with the adsorption of CO\textsubscript{2} in situ can aggressively promote the conversion of CO to H\textsubscript{2} via the WGS reaction (2') above; thus, the methanation reaction is kept at a minimum, while the CO contaminant in the final product is extremely low. The simulations (see Table 1) with HAMR using M\&PCMS membranes at temperatures from 300-400\(^{\circ}\text{C}\) indicate that heptane steam reforming benefits significantly from being carried out in such a reactor. As noted in Table 1, the H\textsubscript{2} yield in the proposed reactor system (defined as the mol of H\textsubscript{2} produced per mol of heptane fed) is many times higher than the corresponding yield of a PBR containing the same amount of catalyst and operating with the same feed as the HAMR system. For a range of operating conditions, the H\textsubscript{2} product contains only a minor amount of CH\textsubscript{4} (\(\sim 3\%\)) and very little CO (<10 ppm), which makes it usable in a fuel cell without further treatment. More importantly, the CO\textsubscript{2} is concentrated in the reject stream and is, therefore, ready for sequestration.

In the simulations, the naphtha reforming reaction was taken to be irreversible. This is the assumption also made in prior studies (Chen et al. (2003) AIChE J. 49:1250, Chen et al. (2003) Ind. Eng. Chem. Res. 42:6549, and Chen et al. (2004) Ind. Eng. Chem. Res. 43:1323) under similar pressure and temperature conditions. The primary effect of H\textsubscript{2} removal through the CMS membrane is its influence on the reaction rate. The reaction rate for heptane reforming has a non-monotonic dependence on H\textsubscript{2} partial pressure (Tøttrup (1982) Appl. Catal. 4:377), i.e.; there is a certain value of H\textsubscript{2} partial pressure that maximizes the rate. Removing H\textsubscript{2} from the reactor through the membranes has the effect in that it maintains the H\textsubscript{2} pressure everywhere in the reactor at or near this optimum level, thus favorably impacting the rate of H\textsubscript{2} production. In fact, the thermodynamic simulations indicate that equilibrium limitations arise for temperatures less than \(400^{\circ}\text{C}\), (although in the reactor simulations, this has not been taken into consideration, since the published rate data do not account for such effects). Under such conditions, additional beneficial effects from the HAMR system are expected, since removing the H\textsubscript{2} tends to shift the reaction equilibrium towards the product side. It is the synergy between adsorbent and membrane that makes it possible to attain CO levels in the H\textsubscript{2} product <10 ppm. The ability to attain very high H\textsubscript{2} yields at low temperatures (<400\(^{\circ}\text{C}\)) vs. the significantly higher temperatures normally practiced in conventional reformers has two additional advantages. One such advantage involves lowering the rate of coke production, and, the potential for catalyst deactivation. The other relates to energy savings (since the feed mixture needs to be heated to a lower temperature), and potentially to the ability to utilize waste heat that may be available in the fuel-gas exhaust of the power producing devices (fuel cells, internal combustion engines, turbines, etc.).

Novel CMS Membranes

CMS membranes represent a “next generation” membrane material, because they vastly improve on the limits of the selectivity vs. permeability relationship set by the polymeric membranes for gas separations. However, in the past, these membranes have been limited purely to an academic novelty.
for three primary reasons, specifically: (i) they suffer several process-related problems including membrane performance deterioration due to temporary and/or permanent poisoning by organics and other impurities, (ii) they are very fragile, when unsupported (as hollow fiber/tubular products), and (iii) they can be very costly given the high performance polymers generally required as precursors. M&P recently developed a commercially viable CMS membrane based upon the R&D work by USC. To do so required innovative solutions to the above application-related barriers. To overcome the fragility and cost problems, the M&P CMS membrane consists of an ultrathin (0.5 to 3 µm thick) CMS layer supported on M&P high performance, high-strength hollow-fiber ceramic membranes (see FIG. 31). In the design, the tube spacing can be arbitrarily selected to maintain the flexibility of the reactor design, if the catalyst is packed in the shell side. For applications >300°C in the presence of steam, graphite seals with ceramic-glass potting ends are utilized. Membrane H₂ permeances ranging from 0.8 to >5 m³/m²/hr/bar (27 to 168 scfh/ft² at 10 bar) have been demonstrated. Selectivities for H₂ to N₂ are 25 to >100 even at temperatures up to 400°C. Nitrogen is used here to represent gas components rejected by this CMS membrane, including CO₂ and CO and light hydrocarbons. Water, as H₂O, is permeable through the membrane. A typical permeance vs. temperature for H₂ and N₂ is presented in FIGS. 32a and 32b as well as Table 2. The H₂ permeance increase is consistent with activated diffusion via molecular sieving. The maximum in selectivity is due to the N₂ permeance, which at low temperatures displays Knudsen type diffusivity (i.e., decreases with temperature) but at higher temperatures becomes activated as molecular sieving begins to dominate (about 150-400°C for this membrane). As is well-known, carbon, particularly microporous carbon, reacts with steam at sufficiently high temperatures. Although 180 to 400°C is generally considered low for carbon steam gasification, long-term thermal and hydrothermal stability testing has been conducted to demonstrate the CMS/C membrane suitability for the proposed reaction environment. FIG. 33 shows the H₂ permeance and H₂/N₂ selectivity of one of the membranes in a hydrothermal stability test conducted at 220°C in a 25-day test run (other tests indicate similar hydrothermal stability at 350°C). The test result demonstrates the hydrothermal stability of the CMS membrane. In addition, although porous carbon poisoning by organic vapors is well-known, it can be prevented by operation at high temperatures, e.g., >200°C, as shown in FIG. 34. Thus far, no other membrane has offered a similar functional performance in this intermediate temperature range (180-400°C). The temperature range is too high for even the most advanced polymer-based membranes. As for inorganic membranes (e.g., silica, zeolite, and others), operating temperatures >>300°C are required to achieve appreciable (economical) permeances. The cost of the CMS membranes is $800/m² ($80/ft²), which is significantly lower than the cost of competing (e.g., Pd) membranes.

### Table 2

<table>
<thead>
<tr>
<th>Part ID</th>
<th>Temperature [°C]</th>
<th>H₂ Permeances [m³/m²/hr/bar]</th>
<th>α-H₂/N₂</th>
<th>α-H₂/CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ-142322</td>
<td>140</td>
<td>1.21</td>
<td>69</td>
<td>28</td>
</tr>
</tbody>
</table>

Adsorbent

In some embodiments, the HAMR system utilizes LDH adsorbents, which have emerged as standard CO₂ adsorbents for high temperature applications, i.e., up to ~400°C. Although many different compositions of LDH can be formulated, one example is Al₆(OH)₁₄[CO₃]₀.₃. According to the literature and prior studies (Yang et al. (2004) Ind. Eng. Chem. Res. 43:4559), about 1.5 to 2.0 wt % CO₂ can be adsorbed with this type of adsorbent at the proposed temperature. Preliminary simulations indicate that this existing hydroxide adsorbent is adequate for application in the HAMR system.

### Design Simulations

The performance of the HAMR system depends upon many system/intrinsic and operating parameters. Key system intrinsic parameters include catalyst reaction rate, H₂ permeation rate, adsorption capacity vs. pressure, catalyst and adsorbent volumes, and their relative ratio. The operating variables include temperature and pressure of the reactor, contact time, and membrane (steam) purge rate. The mathematical model based upon the existing system and intrinsic parameters has produced outstanding reforming performance. This design tool allows defining of a suitable range of the operating variables for a given application and generation of performance vs. time information for determining when the adsorbent requires pressure swing desorption for regeneration. Further, mathematical simulations can be performed to incorporate both adsorption and desorption steps to determine the net H₂ yield and purity for the proposed application and for process optimization and economic analysis.

### Example III

A High Efficiency, Low Temperature Reformer for Hydrogen Production

Introduction


### Table 2-continued

<table>
<thead>
<tr>
<th>Part ID</th>
<th>Temperature [°C]</th>
<th>H₂ Permeances [m³/m²/hr/bar]</th>
<th>α-H₂/N₂</th>
<th>α-H₂/CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ-149834</td>
<td>220</td>
<td>1.1</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>DZ-148620</td>
<td>220</td>
<td>1.1</td>
<td>85</td>
<td>85</td>
</tr>
</tbody>
</table>

Other Membranes

DZ-193454 35 19.2 1.9 Ethane: 18.0 1.2 Iso-Butane: 2.39 He/S: 0.75
behavior of the HAMR system is compared with the conventional system. The reactor is assumed that the reactor operates isothermally, that external transport limitations for the catalyst, and internal or mass transfer resistances are negligible for the transport of the products through the membrane as well as for the catalysts, and that the reactor operates isothermally, that external transport limitations for the adsorbent, are accounted for by the overall rate coefficients. Moreover, plug-flow conditions are assumed that the reactor operates isothermally, that external transport limitations for the adsorbent, are accounted for by the overall rate coefficients. Moreover, plug-flow conditions are assumed for the various reactor configurations, as previously noted. For the methane steam reaction, a catalytic reaction system was investigated. This HAMR system exhibited behavior that is more advantageous than either the MRs or ARs, in terms of the attained yields and selectivities.

A mathematical model for the HAMR system is presented and analyzed for a range of temperature and pressure conditions without any intention to be bound by such theory. The behavior of the HAMR system is compared with the conventional packed bed reactor, as well as an MR and an AR system. Kinetics of Methane Steam Reforming

For the methane steam reaction, a catalytic reaction scheme first proposed by Xu and Froment (1989) J. Phys. Chem. 93: 35 88) is utilized. This scheme has found widespread application. According to Xu and Froment (see also El Mansha et al. (2009) Chem. Eng. Sci. 45: 491, and Nam et al. (2000) Korean J. Chem. Eng. 17: 288), the methane steam reforming reaction consists of two major endothermic reforming reaction steps, together with the exothermic WGS reaction (see Table 1), with the overall reaction being highly endothermic. The rate expressions, heats of reaction, and thermodynamic constants for the three reaction steps are shown in Table 1. The kinetic parameters, as reported by Xu and Froment, are shown in Table 2.

| Table 1 |
| Rate Expressions and Thermodynamic Properties for the Methane-Steam-Reforming Reaction$^a$$^b$ |

<table>
<thead>
<tr>
<th>i reaction</th>
<th>rate expression</th>
<th>heat of reaction at 298 K, $\Delta H_{f}^{\circ}$ (kJ/mol) constant, $K_{eqi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CH₄ + H₂O $\rightarrow$ CO + 3 H₂</td>
<td>$r_1 = \frac{(k_1/RT)^2(PH_2O - P_H_2)/ DEN)}{(P_{H_2}/P_{CO}K_{eq1})}$</td>
<td>206.1</td>
</tr>
<tr>
<td>2 CO + H₂O $\rightarrow$ CO₂ + H₂</td>
<td>$r_2 = \frac{(k_2/RT)^2(PH_2O - P_H_2)/ DEN)}{(P_{H_2}/P_{CO}K_{eq2})}$</td>
<td>-41.15</td>
</tr>
<tr>
<td>3 CH₄ + 2H₂O $\rightarrow$ CO₂ + 4 H₂</td>
<td>$r_3 = \frac{(k_3/RT)^2(PH_2O - P_H_2)/ DEN)}{(P_{H_2}/P_{CO}K_{eq3})}$</td>
<td>164.9</td>
</tr>
</tbody>
</table>

$^a$DEN $= 1 + K_{cat, CO} + K_{cat, H_2} + K_{cat, CH_3} + K_{cat, H_3}/P_{H_2O}$

$^b$Kinetic parameters for the Methane-Steam-Reforming Reaction$^a$

<table>
<thead>
<tr>
<th>kinetic parameter</th>
<th>preexponential terms, $k_{pre}, K_{pre}$</th>
<th>activation energies or heats of chemisorption, $E_{a}, \Delta H_{a}^{\circ}$ (kJ/mol) units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$4.225 \times 10^{15}$</td>
<td>240.1 kmol $\cdot$ bar$^{0.5}$/kg of catalyst/h</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$1.955 \times 10^{2}$</td>
<td>67.13 kmol/kg of catalyst/h/bar</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$1.020 \times 10^{15}$</td>
<td>243.9 kmol $\cdot$ bar$^{-0.5}$/kg of catalyst/h</td>
</tr>
<tr>
<td>$K_{CO}$</td>
<td>$8.23 \times 10^{-5}$</td>
<td>$-70.65$ bar$^{-1}$</td>
</tr>
<tr>
<td>$K_{H_2}$</td>
<td>$6.12 \times 10^{-9}$</td>
<td>$-82.90$ bar$^{-1}$</td>
</tr>
<tr>
<td>$K_{CH_4}$</td>
<td>$6.65 \times 10^{-4}$</td>
<td>$-38.83$ bar$^{-1}$</td>
</tr>
<tr>
<td>$K_{H_2O}$</td>
<td>$1.77 \times 10^{0}$</td>
<td>88.68 bar$^{-1}$</td>
</tr>
</tbody>
</table>

Formation rates for the H₂, CO, and CO₂ products and the disappearance rates for CH₄ and H₂O are given by the following equations:

35. $R_{H_2} = 3r_1 + r_2 + 4r_3$

36. $R_{CO} = r_1 - r_2$

37. $R_{CO_2} = r_1 + r_3$

38. $R_{CH_3} = r_1 + r_3$

39. $R_{H_2O} = r_1 - r_3 - 2r_3$

Mathematical Model of the HAMR System

A schematic of the HAMR system is shown in FIG. 35. In this figure, the catalyst and adsorbent are packed in the exterior of the membrane (signified by the superscript P, or the permeate side), with additional adsorbent also packed in the interior of the membrane volume (signified by the superscript F, or the feed side). There are, of course, a number of other potential reactor configurations, as previously noted. For example, the catalyst may be loaded in the feed side, while the adsorbent may also be loaded in the permeate side, or the catalyst and adsorbent may only be loaded in the feed side, with no adsorbent or catalyst being present in the permeate side, which is the configuration that is analyzed here. To simplify matters, in the development of the model, it is assumed that the reactor operates isothermally, that external mass transfer resistances are negligible for the transport through the membrane as well as for the catalysts, and that internal diffusion limitations for the catalyst, and internal or external transport limitations for the adsorbent, are accounted for by the overall rate coefficients. Moreover, plug-flow conditions are assumed to prevail for both the interior and exterior membrane volumes as well as ideal gas law conditions.
In the simulations, the experimentally measured transport characteristics of a microporous SiC membrane (Ciora et al. (2004) Chem. Eng. Sci. 59:4957) is utilized. These membranes have been shown previously to be thermally and hydrothermally stable under conditions akin to the steam reforming reaction conditions (Ciora et al. (2004) Chem. Eng. Sci. 59:4957). Further details about their preparation and characterization can be found in the original publication. The SiC membranes are highly permeable toward hydrogen, with gases with larger kinetic diameters permeating only by Knudsen diffusion through membrane pinholes and cracks (Ciora et al. (2004) Chem. Eng. Sci. 59:4957). Mass transfer through the porous membrane is described by the following empirical equation:

\[ F_j = U_j (P_j^f - P_j^p) \]  

where \( F_j \) is the molar flux (mol/m²s), \( P_j^f \) the partial pressure of component \( j \) on the membrane feed side (bar), \( P_j^p \) the partial pressure of component \( j \) on the membrane permeate side (bar), and \( U_j \) the membrane permeance for component \( j \) (mol/m²-bar-s). Equation 6 is, of course, a simplified empirical expression for describing flux through a nanoporous membrane for which the size of the pores approaches that of the diffusing molecules.


\[ \frac{dC_{seq}}{dt} = \frac{m_{CO_2}^b - b_{CO_2} P_{CO_2}}{T + b_{CO_2} P_{CO_2}} \]

where \( C_{seq} \) is the adsorption equilibrium CO₂ concentration on the adsorbent (mol/kg) corresponding to the prevailing gas phase concentration, \( C_2 \) the existing adsorbed CO₂ concentration (mol/kg), and \( k_a (s^{-1}) \) is a parameter that "lumps" together the effects of external and intraparticle mass transport and the sorption processes and that, as a result, is often a strong function of temperature and pressure (Ding and Alpay (2000) Chem. Eng. Sci. 55:3461) although, typically, in modeling, it is taken as temperature/pressure-independent. To calculate \( C_{seq} \), the data reported by Ding and Alpay ((2000) Chem. Eng. Sci. 55:392927 and (2000) Chem. Eng. Sci. 55:3461) for CO₂ adsorption on potassium-promoted LDH are utilized. Their data show that the CO₂ adsorption on this adsorbent follows a Langmuir adsorption isotherm under both dry and wet conditions, described by the following equation:

\[ C_{seq} = \frac{m_{CO_2}^b - b_{CO_2} P_{CO_2}}{T + b_{CO_2} P_{CO_2}} \]

where \( m_{CO_2}^b \) (mol/kg) is the total adsorbent capacity and \( b_{CO_2} \) (bar⁻¹) the adsorption equilibrium constant, which is described by the van’t Hoff equation:

\[ b_{CO_2} = \frac{\Delta H_{ads}}{RT_0} \exp[-\Delta L/R(1/T-1/T_0)] \]

The heat of adsorption, \( \Delta H_{ads} \) (kJ/mol), under wet conditions for a region of temperatures from 481 to 755 K is calculated to be ≈17 kJ/mol, while \( b_{CO_2} \) at 673 K is equal to 23.6 bar (Ding and Alpay (2000) Chem. Eng. Sci. 55:3461). Equations 7 and 9 must be complemented by initial and boundary conditions. For simplicity, it is assumed that the reactor, prior to the start of the reaction/adsorption step, has undergone a start-up procedure as described by Ding and Alpay ((2000) Chem. Eng. Sci. 55:3929) that involves (i) heating the reactor to the desired temperature under atmospheric pressures by feeding H₂ on the reactor feed side and the chosen sweep gas on the permeate side, (ii) supplying water to the system so that the feed H₂O/H₂ ratio is the same as the H₂O/CH₄ ratio to be used during the reaction step, (iii) pressurizing the feed and permeate sides to the desired pressure conditions, and (iv) switching from H₂ to CH₄ to initiate the reaction/adsorption step. In the simulations, the conditions prevailing at the start of step (iv) are those prevailing at steady state during step (iii).

\[
\text{at } V = 0; \quad \frac{\partial \phi_j^F}{\partial V} = -\frac{\mu_j^F (\phi_j^F - \phi_j^I)}{A^F D_m^F} \quad (12a)
\]

\[
\text{at } V = V_l; \quad \frac{\partial \phi_j^F}{\partial V} = 0 \quad (12b)
\]

where \(\phi_j^F\) is the mole fraction of species \(j\) at the permeate side at the start of step (iv) are those prevailing at steady state during step (iii). In addition, during step (iv) the following boundary conditions prevail in the permeate side:

\[
\text{at } V = 0; \quad \frac{\partial \phi_j^F}{\partial V} = -\frac{\mu_j^F (\phi_j^F - \phi_j^I)}{A^F D_m^F} \quad (16a)
\]

\[
\text{at } V = V_k; \quad \frac{\partial \phi_j^F}{\partial V} = 0 \quad (16b)
\]

where \(x_j^F\) is the mole fraction, \(x_j^I\) the inlet mole fraction for species \(j\) on the permeate side, and \(u_j^F\) the superficial flow velocity (m/s) at the inlet. Because no adsorbent or catalyst is present in the permeate side, any potential pressure drop is ignored.

The reactor conversion (based on methane, which is typically the limiting reagent) is defined by the following equation:

\[
x_{CH_4} = \frac{n_{CH_4,i} - (n_{CH_4,e} + n_{H_2,e})}{n_{CH_4,i}} \quad (17)
\]

where \(n_{CH_4,i}^F\) is the inlet molar flow rate of \(CH_4\) and \(n_{CH_4,e}\) and \(n_{H_2,e}\) are the methane molar flow rates at the exit of the reactor feed and permeate sides correspondingly (mol/s). The yield of product hydrogen, defined as the fraction of moles of methane fed into the reactor that have reacted to produce hydrogen, is given by the following equation:

\[
y_{H_2} = \frac{1}{4} \left( n_{H_2,e} - n_{H_2,i} - n_{CO_2,i} \right) \quad (18)
\]

where \(n_{H_2,e}\) and \(n_{H_2,i}\) are the hydrogen molar flow rates at the exit and inlet of the reactor feed and permeate sides respectively (mol/s). \(Y_{H_2}\) when all of the methane have reacted completely to produce \(CO_2\) and \(H_2\). Eqs. 6-18 can be written in dimensionless form by defining the following variables and groups:

\[
\begin{align*}
\tau_a &= (U_o)^{-1}; \quad \tau_r = \frac{V_r}{A^F A_0^F}; \quad \gamma = \frac{\phi_a}{\phi_r}; \quad \eta = \frac{\phi_r}{\phi_a}; \quad \phi^F = \frac{\phi^I}{\phi^F}; \\
\psi^F &= \frac{\phi^F}{\psi^F}; \quad \phi^I = \frac{\phi^I}{\psi^F}; \quad \phi_j^I = \frac{\phi_j^I}{\psi^F}; \\
\omega &= \frac{P^I}{P^F}; \quad \alpha_j = \frac{MW_j}{MW_CCH_4}; \quad \phi_j^I = \phi_j^I \frac{P^F}{P^I}; \quad \phi_j^F = \phi_j^F \frac{P^I}{P^F}; \quad \tau = \kappa_t; \\
\delta_j &= \frac{U_j}{U_0}; \quad K_{en} = \frac{K_{en}}{(P_e^F)^2}; \quad K_{CO} = \frac{K_{en}}{P_0^F}; \\
D_{m} &= \frac{A^F (1 - \phi^I) P_{e} U_k^2 \rho_k \rho C_{CO}}{A^F (P_k^F)^2 (P_0^F)^2}; \quad \phi^I = \frac{\phi^I}{U_0 \rho_k \rho C_{CO}}; \\
D_{m} &= \frac{A^F (1 - \phi^I) P_{e} U_k^2 \rho_k \rho C_{CO}}{A^F (P_k^F)^2 (P_0^F)^2}; \quad \phi^F = \frac{\phi^F}{U_0 \rho_k \rho C_{CO}}.
\end{align*}
\]
where in dimensionless form:

\[ G_{CO2} = (\theta_{CO2} - \theta_r) \]

\[ \theta_{eq} = \frac{\beta_{CO2} \theta_r \Psi}{1 + \beta_{CO2} \theta_r \Psi} \]

and \( R'_i \) are dimensionless forms of \( R_i \), which are described by Eqs. 1-5, with the dimensionless forms of the rates \( r'_1-r'_3 \) shown in Table 3.

### TABLE 3

<table>
<thead>
<tr>
<th>i reaction</th>
<th>rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 )</td>
<td>( r_i = \left(1 - \frac{1}{\beta_{\text{H}_2} \Psi} \right) \left[ \frac{\text{CH}<em>4 \Psi}{\beta</em>{\text{H}_2} \Psi (\text{CH}_4 \text{H}<em>2 \text{O} \Psi) \theta</em>{eq}} \right] )</td>
</tr>
</tbody>
</table>

The system of coupled nonlinear partial differential Eqs. (19)-(24) and accompanying boundary conditions has been solved in MATLAB using the method of lines (Schiesser 1991) The Numerical Method of Lines: Integration of Partial Differential Equations, Academic Press, San Diego and Vande Wouwer et al. (2004) Ind. Eng. Chem. Res. 43:3469). The system of partial differential equations was converted to a set of ordinary differential equations by discretizing the spatial derivative in the \( \eta \) direction using a five-point-biased upwind finite-difference scheme to approximate the convective term. A fourth-order central-difference scheme has been used to approximate the diffusive term. For finite differences, the reactor volume is divided into \( n \) sections with \( n+1 \) nodes. The initial value ordinary differential equations and other explicit algebraic equations at a time \( r \) are simultaneously solved using ode45.m, a MATLAB built-in solver for initial value problems for ordinary differential equations.

### Results and Discussion

The behavior of the HAMR and AR at two temperatures (400 and 480°C) for which experimental data for the adsorption/reaction step are those prevailing during step 3 previously described. In addition, the following boundary conditions also apply:

- for \( r > 0 \), at \( \eta = 0 \):
  - \( \Psi' = 1 \), \( \Psi'' = 1 \)
  - \( \alpha = 1 \), \( \beta = 1 \)

- for \( r > 0 \), at \( \eta = 1 \):
  - \( \Psi'' = 0 \)
  - \( \alpha'' = 0 \)

where \( s = \Sigma \Psi'' / \Sigma \alpha'' = \lambda (\Sigma \Psi'' / \Sigma \alpha'') \) is the sweep ratio for the MR.

FIG. 37 shows the CO content of the hydrogen product in the feed side (less hydrogen was produced there because the adsorbent no longer removed the CO) and also on the product purity for both the HAMR and AR systems (see Table 4 for the CO content of the hydrogen product).

The effect of using an adsorbent with improved characteristics is shown in FIG. 42. The hydrogen yields for the HAMR and AR systems were compared for three values of \( A \), one corresponding to the adsorbent of Ding and Alpay ((2000) Chem. Eng. Sci. 55:3461) (for the reactor temperature and pressure conditions utilized, this corresponds to \( \Lambda = 2.67 \)) and

<table>
<thead>
<tr>
<th>Table 4 - continued</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>( b_{\text{CH}_2} )</td>
</tr>
<tr>
<td>( d_P )</td>
</tr>
<tr>
<td>( D_{\text{sr}} )</td>
</tr>
<tr>
<td>( H_{\text{r}} )</td>
</tr>
<tr>
<td>( k )</td>
</tr>
<tr>
<td>( m_{\text{CH}_2} )</td>
</tr>
<tr>
<td>( \rho_{\text{r}} )</td>
</tr>
<tr>
<td>( \rho_{\text{g}} )</td>
</tr>
<tr>
<td>( s )</td>
</tr>
<tr>
<td>( T )</td>
</tr>
<tr>
<td>( T' )</td>
</tr>
<tr>
<td>( T'' )</td>
</tr>
<tr>
<td>( U_{\text{g}} )</td>
</tr>
<tr>
<td>( v_{\text{r}} )</td>
</tr>
<tr>
<td>( \alpha_{\text{r}} )</td>
</tr>
<tr>
<td>( \beta_{\text{r}} )</td>
</tr>
<tr>
<td>( \rho_{\text{CO}} )</td>
</tr>
<tr>
<td>( \gamma )</td>
</tr>
<tr>
<td>( A )</td>
</tr>
</tbody>
</table>
two other cases with corresponding A values 5 and 10 times larger. A more effective adsorbent significantly expanded the “time window” of operation for both the AR and HAMR systems before regeneration must commence. It also significantly increased the hydrogen yields attained.

The effect of membrane transport characteristics is shown in FIG. 43, where the reactor yields corresponding to four different membranes (i.e., four different values of Ω) are shown. For the SiC membrane used in the simulations, Ω=1.54. The other three membranes had Ω values that were 0.333, 0.5, and 2 times the base Ω value (because Ω is inversely proportional to permeance, these Ω values correspond to permeances that were 3, 2, and 0.5 times that of the base case corresponding to Ω=1.54). The HAMR system hydrogen yields did benefit from increased hydrogen permeance, but the effect saturated beyond a certain value. FIG. 44 shows the effect that Ω has on hydrogen recovery. As expected, increasing the hydrogen permeance had a very beneficial effect on hydrogen recovery, with very high hydrogen recoveries (~87%) attained for 0.333 times the base case Ω. FIG. 45 shows the effect of the sweep ratio on the hydrogen yield of the HAMR system. Increasing the sweep ratio improved the reactor performance; however, the effect saturated quickly, as shown in FIG. 45. FIGS. 46 and 47 show the behavior of the two systems at 400° C. FIG. 46 shows the hydrogen yield, while FIG. 47 presents the time-averaged CO (wet basis, in ppm) content for both the HAMR and AR systems. The average CO purity, (yCO), at the given operating time t, is calculated by:

\[
\langle y_{CO} \rangle = \frac{\int_{0}^{t} \left( \frac{P_{CO}}{RT} \right)_{inlet} \, dt}{\int_{0}^{t} \left( \frac{P_{CO}}{RT} \right)_{outlet} \, dt} \text{ for HAMR;}
\]

\[
\langle y_{CO} \rangle = \frac{\int_{0}^{t} \left( \frac{P_{CO}}{RT} \right)_{inlet} \, dt}{\int_{0}^{t} \left( \frac{P_{CO}}{RT} \right)_{outlet} \, dt} \text{ for AR}
\]

The conditions in the figure were such that for a good fraction of the adsorption/reaction cycle for the HAMR system, the CO content in the hydrogen product stayed below 50 ppm (140 ppm on a dry basis).

Conclusions

A novel reactor system, termed HAMR, for hydrogen production through methane steam reforming was investigated. The HAMR combines the reaction and membrane separation steps with adsorption on the membrane feed or permeate sides. The HAMR system is of potential interest to pure hydrogen production for PEM fuel cells for various mobile and stationary applications. The reactor characteristics have been investigated for a range of temperature, pressure, and other experimental conditions relevant to the aforementioned applications and compared with the behavior of the traditional packed bed reactor, the conventional MR, and an AR. The HAMR outperformed all of the other more conventional reactor systems. It exhibited enhanced methane conversion, hydrogen yield, and product purity and showed good promise for reducing the hostile operating conditions of conventional methane steam reformers and for meeting the product purity requirements for PEM operation. The performance of the HAMR system depended on the various operating parameters, including the reactor space time, the temperature, and the membrane and adsorbent properties. Use of more effective adsorbents, for example, resulted in increased yields and longer operational windows. More highly permeable membranes also increased the reactor yield but, more importantly, also increased the hydrogen recovery ratio. One of the key advantages of the HAMR system over the corresponding AR system (in addition to improvements in yield) is its ability to deliver a product with a significantly lower CO content through the use of membranes, which preferentially allow the permeation of the hydrogen while excluding CO and other reactants and products. This may be the primary reason for adopting such reactors for fuel cell application, where a CO-free product is at a premium.

Example IV

The adsorption equilibrium capacity and rate for the CO₂ affinity adsorbent, hydrotalcite, used in this study were experimentally determined. The lab scale adsorption isotherm study was performed using a gravimetric technique. The adsorption isotherms for CO₂ on hydrotalcite at 250-450° C were determined by measuring the CO₂ uptake data. The experimental data were then fitted with the Langmuir adsorption isotherm as presented in FIG. 48. Table 5 shows the Langmuir parameters obtained by fitting the adsorption data for various temperatures. The transient CO₂ uptake data were measured at each elevated temperature, and then the diffusion coefficients were estimated by fitting acquired experimental data to the solution of the relevant diffusion equation. Table 6 gives the diffusivity data obtained by fitting the experimental data to the diffusion equation for the temperatures studied.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>m_{CO₂, mmol/g sample}</th>
<th>b_{CO₂, kPa⁻¹}</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.337</td>
<td>0.05</td>
</tr>
<tr>
<td>350</td>
<td>0.387</td>
<td>0.088</td>
</tr>
<tr>
<td>450</td>
<td>0.337</td>
<td>0.099</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Df², s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>9.52 x 10⁻⁴</td>
</tr>
<tr>
<td>350</td>
<td>3.42 x 10⁻⁴</td>
</tr>
<tr>
<td>450</td>
<td>6.00 x 10⁻⁴</td>
</tr>
</tbody>
</table>

Kinetic constants for WGS reaction are critical input parameters for the performance simulation of the HAMR. A laboratory scale reactor system was established as shown in FIG. 49 to study the reaction kinetics, which was then employed for the HAMR study. Synthetic feed was prepared from pure gas cylinders with mass flow controllers. The reactor temperature was kept at the target temperature within a constant temperature box. The effluent from the reactor was analyzed with a mass spectrometer after water dropout via condensation.
Three different temperatures were selected, i.e., 205, 225 and 250°C, which covered the temperature range recommended by the catalyst manufacturer for the low temperature shift catalyst. Pressure of the reactor was kept at ~50 psig. The feed composition selected for this study was CO:H2: H2O=1:0.4:0.1:1. W/Fo selected ranged from ~30 to as high as ~467, which spanned a wide operating condition for obtaining representative kinetic parameters. The reaction rate constants obtained experimentally were then used to determine the pre-exponential factor and the activation energy required. The pre-exponential factor and the activation energy determined based upon the operating condition are listed in Table 7. These kinetic parameters were used in the mathematical simulation.

<table>
<thead>
<tr>
<th>TABLE 7</th>
<th>Reaction Rate and Kinetic Parameters for WGS.</th>
</tr>
</thead>
<tbody>
<tr>
<td>r = A exp(-Ea/RT)'</td>
<td>k0 = 1.77E+11</td>
</tr>
<tr>
<td>g - mol/(g cat * hr * bar 0.4)</td>
<td>E = 114.22</td>
</tr>
</tbody>
</table>

Experimental investigations of HAMR systems using CO2 hydrotalcite-type adsorbents and a porous H2 selective membranes (similar to the one shown in Example 1) were also carried out. The behavior of the HAMR and conventional PBR for the WGS reaction for hydrogen production with concomitant CO2 removal were simulated. The adsorption rates and constants were taken from the adsorption studies. The reaction rate constants and the membrane permeances were experimentally determined, as outlined above. The reactor characteristics have been investigated for a range of temperature and pressure conditions and compared with the predictions of the mathematical model. The reactor temperature utilized was 250°C, and a CO:H2:H2O feed ratio of 1:4:1:1 was employed. Steam was used as the sweep gas. FIGS. 51 and 53 show the CO conversion attained by both the PBR and HAMR as a function of time for Wc/F, 300 and 350 (Wc is the total weight of the catalyst). The reactor showed complete conversion, while the adsorbent was still active. After the adsorbent saturated, the conversion settled to the value corresponding to the membrane reactor conditions, which was still significantly higher than the conversion of the PBR system and the corresponding equilibrium.
a catalyst disposed in the chamber for facilitating a reaction of the reactants to produce at least one desired product and at least one by-product, wherein the reaction is a steam reforming reaction;
amembrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane;
an adsorbent disposed in the chamber for adsorbing the by-product; and
an outlet for allowing the desired product to exit the chamber, wherein neither the catalyst nor the adsorbent is disposed in a circulating fluidized bed.

11. The reactor of claim 10, wherein the membrane is a CMS or silicon carbide membrane.

12. The reactor of claim 10, wherein the adsorbent is a hydrotalcite.

13. An apparatus comprising:
at least two reactors, each reactor including:
a chamber;
an inlet for introducing one or more reactants into the chamber;
a catalyst disposed in the chamber for facilitating a reaction of the reactants to produce at least one desired product and at least one by-product, wherein the reaction is a steam reforming reaction;
amembrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane;
an adsorbent disposed in the chamber for adsorbing the by-product; and
an outlet for allowing the desired product to exit the chamber.

14. The reactor of claim 13, wherein the membrane is a CMS or silicon carbide membrane.

15. The reactor of claim 13, wherein the adsorbent is a hydrotalcite.

16. A reactor comprising:
a chamber;
an inlet for introducing one or more reactants into the chamber;
a catalyst disposed in the chamber for facilitating a reaction of the reactants to produce at least one desired product and at least one by-product;
a CMS or silicon carbide membrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane;
an adsorbent disposed in the chamber for adsorbing the by-product; and
an outlet for allowing the desired product to exit the chamber.

17. The reactor of claim 16, wherein the adsorbent is a hydrotalcite.

18. An apparatus comprising at least two reactors of claim 16.

35 a catalyst disposed in the chamber for facilitating a reaction of the reactants to produce at least one desired product and at least one by-product, wherein the reaction is a steam reforming reaction;
amembrane disposed in the chamber for selectively permitting the desired product and the by-product to pass through the membrane;
an adsorbent disposed in the chamber for adsorbing the by-product; and
an outlet for allowing the desired product to exit the chamber.

20. An apparatus comprising at least two reactors of claim 19.

21. A process comprising:
introducing one or more reactants into the reactor of claim 1; contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product;
selectively passing the desired product and the by-product through the membrane;
adsorbing the by-product with the adsorbent; and
withdrawing the desired product from the reactor.

22. The process of claim 21, wherein the process is carried out at 275-700° C.

23. A process comprising:
introducing one or more reactants into each reactor of the apparatus of claim 4;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product in the reactor;
selectively passing the desired product and the by-product through the membrane in the reactor;
adsorbing the by-product with the adsorbent in the reactor; and
withdrawing the desired product from the reactor, wherein the reactors of the apparatus are offset in point of time such that, at all times, the desired product is being withdrawn from at least one of the reactors.

24. The process of claim 23, wherein the process is carried out at 275-700° C.

25. A process comprising:
introducing one or more reactants into the reactor of claim 5;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product; selectively passing the desired product and the by-product through the membrane;
adsorbing the by-product with the adsorbent; and withdrawing the desired product from the reactor.

26. The process of claim 25, wherein the process is carried out at 275-700° C.

27. A process comprising:
introducing one or more reactants into the reactor of claim 8;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product;
selectively passing the desired product and the by-product through the membrane;
adsorbing the by-product with the adsorbent; and withdrawing the desired product from the reactor.

28. The process of claim 27, wherein the process is carried out at 275-700° C.

29. A process comprising:
introducing one or more reactants into the reactor of claim 10;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product;
selectively passing the desired product and the by-product through the membrane;
adsorbing the by-product with the adsorbent; and withdrawing the desired product from the reactor.

30. The process of claim 29, wherein the process is carried out at 275-700° C.
31. A process comprising:
introducing one or more reactants into each reactor of the apparatus of claim 13;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product in the reactor;
selectively passing the desired product and the by-product through the membrane in the reactor;
adsorbing the by-product with the adsorbent in the reactor;
and withdrawing the desired product from the reactor,
wherein the reactors of the apparatus are offset in point of time such that, at all times, the desired product is being withdrawn from at least one of the reactors.

32. The process of claim 31, wherein the process is carried out at 275-700°C.

33. A process comprising:
introducing one or more reactants into the reactor of claim 16;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product;
selectively passing the desired product and the by-product through the membrane;
adsorbing the by-product with the adsorbent; and
withdrawing the desired product from the reactor.

34. The process of claim 33, wherein the process is carried out at 275-700°C.

35. A process comprising:
introducing one or more reactants into each reactor of the apparatus of claim 18;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product in the reactor;
selectively passing the desired product and the by-product through the membrane in the reactor;
adsorbing the by-product with the adsorbent with the adsorbent in the reactor;
and withdrawing the desired product from the reactor,
wherein the reactors of the apparatus are offset in point of time such that, at all times, the desired product is being withdrawn from at least one of the reactors.

36. The process of claim 35, wherein the process is carried out at 275-700°C.

37. A process comprising:
introducing one or more reactants into the reactor of claim 19;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product;
selectively passing the desired product and the by-product through the membrane;
adsorbing the by-product with the adsorbent; and
withdrawing the desired product from the reactor.

38. The process of claim 37, wherein the process is carried out at 275-700°C.

39. A process comprising:
introducing one or more reactants into each reactor of the apparatus of claim 20;
contacting the catalyst with the reactants to facilitate a reaction of the reactants to produce at least one desired product and at least one by-product in the reactor;
selectively passing the desired product and the by-product through the membrane in the reactor;
adsorbing the by-product with the adsorbent in the reactor;
and withdrawing the desired product from the reactor,
wherein the reactors of the apparatus are offset in point of time such that, at all times, the desired product is being withdrawn from at least one of the reactors.

40. The process of claim 39, wherein the process is carried out at 275-700°C.