(51) **International Patent Classification:**
B01J 8/02 (2006.01)   *B01D 53/22* (2006.01)
C01B 3/50 (2006.01)

(21) **International Application Number:**
PCT/US2005/033295

(22) **International Filing Date:**
19 September 2005 (19.09.2005)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
60/611,682   21 September 2004 (21.09.2004)   US

(71) **Applicants** *(for all designated States except US)*: **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US). **WORCESTER POLYTECHIC INSTITUTE** [US/US]; 100 Imstitute Road, Worcester, MA 01609 (US).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **WELLINGTON, Scott, Lee** [US/US]; 5109 Aspen Street, Bellaire, TX 77401 (US). **MATZAKOS, Andreas, Nicholas** [US/US]; 2115 Parkview Lane, Missouri City, TX 77459 (US). **MARDILOVICH, Ivan, Pietrovich** [US/US]; 32A

Boynto, Apt. 4, Worcester, MA 01609 (US). **MA, Yi Hua** [US/US]; 50 Westwood Drive, Worcester, Massachusetts 01609 (US). **ENGWALL, Erik, Edwin** [US/US]; 24 Dean Street ,Apt. 2A, Worcester, MA 01609 (US).

(74) **Agent: TAYLOR, Richard, B.**; Shell Oil Company, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,

[Continued on next page]

(54) **Title:** REACTOR AND PROCESS FOR STEAM REFORMING
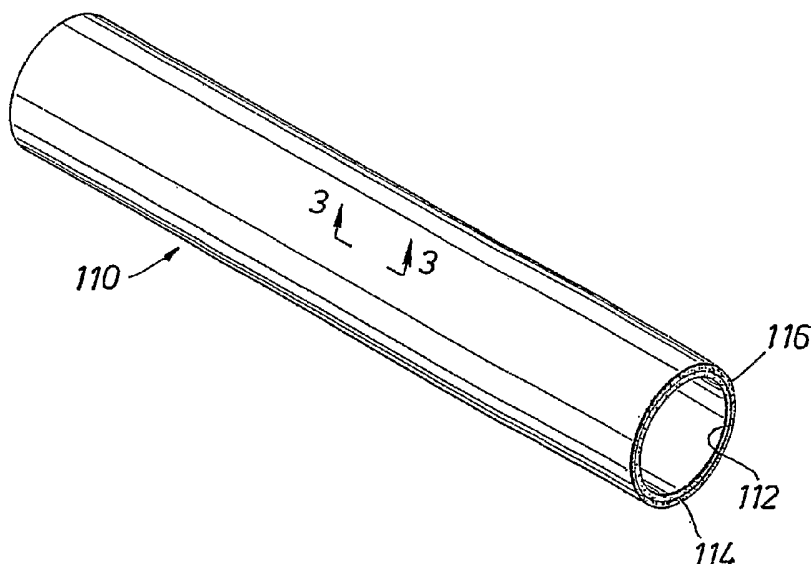
(57) **Abstract:** A hydrogen producing reactor is disclosed. The hydrogen producing reactor has a reaction chamber containing a catalyst bed adapted to produce reaction products containing hydrogen from a hydrogen-producing feedstock. The reaction chamber also includes a hydrogen-selective, hydrogen-permeable gas separation module adapted to receive the reaction products from the catalyst bed and to separate a product stream containing hydrogen from the reaction products. The gas separation module comprises a porous substrate, an intermediate layer located at the porous substrate, and a hydrogen-selective membrane overlying the intermediate layer. The intermediate layer comprises particles and a binder metal, where the binder metal is distributed through out the intermediate layer. A steam reforming process is also disclosed using the disclosed reactor.

RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

REACTOR AND PROCESS FOR STEAM REFORMING

Field of the Invention

This invention relates to a hydrogen producing reactor. The invention further relates

5   to a steam reforming process using said reactor.

Background of the Invention

Purified hydrogen is an important fuel source for many energy conversion devices.

For example, fuel cells use highly purified hydrogen to produce electricity. Chemical

processes, such as steam reforming, are usually operated at high temperature and produce

10   hydrogen as well as certain by-products and impurities. Subsequent purification processes

are required to remove the undesirable impurities to provide hydrogen sufficiently purified

for certain applications, such as a fuel cell.

A majority of the hydrogen-producing chemical processes and subsequent proc-

esses of hydrogen purification occur in separate apparatus. It is advantageous to have a

15   single, compact and more economical apparatus which combines a hydrogen-production

reactor, such as a steam reformer, with a hydrogen separation and purification device

which is operable at high temperature.

U.S. 5,997,594, issued December 7, 1999, discloses a steam reformer which con-

tains a hydrogen purification palladium metal membrane module.

20   The effective life of a typical composite gas separation module having a hydrogen-

selective metal membrane bonded to a porous substrate often is limited by diffusion of sub-

strate components into the membrane which decreases the hydrogen permeability of the

membrane. The rate of diffusion of the substrate components is greatest when the substrate

is at or above its Tamman temperature. A metal lattice at its Tamman temperature is sub-

25   jected to considerable thermal (atomic) vibration. If there is an interface between two met-

als, such thermal vibration significantly increases the mobility of metal atoms and their

consequent diffusion. The Tamman temperature of a material is equal to one-half of its

melting point temperature in Kelvin. For example, in the case of a hydrogen-selective pal-

ladium membrane on a stainless steel substrate, palladium and stainless steel have melting

30   point temperatures of 1552°C (1825 K) and 1375-1400°C (1648-1673 K), respectively.

The corresponding Tamman temperatures are about 640°C (913 K) and 550-560°C (823-

833 K), respectively. The lower of these Tamman temperatures determines the tempera-

ture where a significant increase in intermetallic diffusion can occur. Accordingly, at tem-

peratures around 550°C considerable thermal vibration and diffusion of stainless steel substrate components into a palladium membrane can be expected in such a composite gas separation module. The alloy created by the diffusion of stainless steel substrate components into a palladium membrane can have reduced hydrogen permeability.

5   Typical hydrogen-selective metal membranes used in hydrogen gas separation modules must be free of defects and/or pinholes that breach the metal layer to prevent the migration of undesired gases through the metal membrane. Thick hydrogen-selective metal membranes, e.g., palladium membranes, generally are very expensive. Porous substrates used in the fabrication of composite gas separation modules can have broad pore

10   size distributions and/or rough surfaces such that thick gas-selective membranes can be needed to effectively separate gases. Generally, as the thickness of the gas-selective membrane increases, gas flux through the gas separation module decreases. However, in ordinary metal membranes operated at high temperature, intermetallic diffusion between the porous substrate and metal membrane will occur. This diffusion will cause deterioration of

15   the hydrogen flux. Therefore, a need exists for a hydrogen gas separation module which is durable for a high temperature operation by preventing intermetallic diffusion while being thin enough to provide sufficiently high fluxes of hydrogen gas.

Typical reactors operated at high temperatures usually are made of metals which would withstand high temperature for producing hydrogen and high pressure and which are

20   relatively expensive. It would be desirable if lower temperatures could be used so that lower-cost metallurgy can be utilized for the reactor. Therefore, there is a need for providing for the reactors with more uniform heating and having more control over temperatures at various points to avoid hot spots.

Furthermore, it would be desirable in the art to provide an integrated hydrogen-

25   production and purification reactor design for producing high purity hydrogen having carbon and carbon oxides separated while having minimal production of NO_x within the integrated reactor. It would also be desirable to provide the modularity needed at bulk-hydrogen production scales so that a producer can match the desired capacity by installing multiple reactor units of the specific design. This is more cost-effective than either trying

30   to scale up or down the existing large box furnace reactor designs or building several thousand single-tube reactors. It would also be desirable to employ less volume than conventional processes by intensifying the process and using less catalyst and smaller heater space. Furthermore, if the process produced CO_2 in higher concentrations and greater pu-

rity than other processes in the art, and the CO_2 could be sequestered for other uses, it would be extremely desirable. Such an integrated system would demonstrate far greater efficiency than any power generating system currently available.

Summary of the Invention

5   In one embodiment, the invention is directed to a reactor, comprising:

a)   a reaction chamber comprising:

a catalyst bed adapted to produce reaction products comprising hydrogen gas from a hydrogen-producing feedstock; and

b)   at least one hydrogen-selective, hydrogen-permeable gas separation module

10   adapted to receive the reaction products from the catalyst bed and to separate the reaction products into (1) a product stream comprising hydrogen and (2) a byproduct stream, wherein the gas separation module comprises:

(i)   a porous substrate;

(ii)   an intermediate porous metal layer overlying the porous substrate;

15   and

(iii)   a hydrogen-selective membrane overlying the intermediate porous metal layer.

In another embodiment the present invention is directed to a steam reforming process for the production of hydrogen, comprising:

20   (a) reacting steam with a hydrogen-producing feedstock at a temperature of from 200°C to 700°C and at a pressure of from 0.1 MPa to 20 MPa in a steam reforming reaction chamber containing a reforming catalyst to produce a mixture of hydrogen and carbon dioxide with a lesser amount of carbon monoxide; and

(b) separating hydrogen from said reaction chamber and from said carbon dioxide

25   and said carbon monoxide with a hydrogen-selective, hydrogen-permeable gas separation module, where the gas separation module comprises:

(i)   a porous substrate;

(ii)   an intermediate porous metal layer overlying said porous substrate; and

30   (iii)   a hydrogen-selective membrane overlying the intermediate porous metal layer.

Brief Description of the Drawings

Figure 1 is a schematic diagram of the novel hydrogenproducing reactor with cata-
lyst section, and a hydrogen gas separation tube placed in order from the outside in.

Figure 2 is a schematic diagram of one of the configurations of the hydrogen gas

5   separation tubes useful for the present hydrogen-producing reactor and process.

Figure 3 is a cross-section representation of a composite hydrogen gas separation
module in the present reactor.

Figure 4 is schematic diagram of a multi-tubular, distributed combustion heated,
radial flow, membrane, steam reforming reactor in accordance with the invention. Some of

10   the inlet and outlet streams of the membrane and distributed combustion tubes have been
omitted for simplicity.

Figure 5 is a cross section of the shell of the multi-tubular, distributed combustion
heated, radial flow, membrane reactor shown in Figure 4.

Figures 6A and 6B are schematic diagrams of a "closed ended" and of an "open

15   ended" distributed combustion ("DC") tubular chamber used to drive the reforming reac-
tions in the process and apparatus of the present invention.

Figure 7 is a schematic diagram of a multi-tubular, DC heated, axial flow, mem-
brane steam reforming reactor in accordance with the invention.

Figure 8 is a cross section of the shell of the multi-tubular, distributed combustion

20   heated, axial flow, membrane reactor shown in Figure 7.

Figures 9A & 9B and 9C & 9D are schematic diagrams of two baffle configurations
which can be employed to increase the contact of the reactant gases with the catalyst in a
multi-tubular, distributed combustion-heated, axial flow, membrane reactor in accordance
with the invention.

25   Figures 10, 11, 12, and 13 are top cross section views of the shells of other em-
bodiments of the multi-tubular, distributed combustion heated, axial flow, membrane,
steam reforming reactors of the invention.

Figure 14 is a simplified flow diagram of the distributed combustion membrane
steam reformer fuel hybrid power system.

30

Detailed Description of the Invention

The invention relates to a reactor comprising a reaction chamber and a gas separa-
tion module. It provides a new apparatus and process for producing high purity hydrogen

from a hydrogen producing feedstock, said process being accomplished in one reactor, constantly removing pure hydrogen, and optionally using distributed combustion as a heat source which provides great improvements in heat exchange efficiency and load-following capabilities to drive the steam reforming reaction. The hydrogen-selective gas separation

5   module has thinner dense gas-selective membrane producing higher rates of gas flux, e.g. hydrogen flux, while durability (including reduced diffusion of substrate components), hydrogen permeation as well as selectivity are maintained or improved. In another embodiment, the invention is also a zero emission hybrid power system wherein the produced hydrogen is used to power a high-pressure internally or externally manifolded fuel cell, such

10   as a molten carbonate fuel cell. The design can be a membrane steam reforming reactor fueled hybrid system makes it possible to capture high concentrations of CO_2 for sequestration or use in other processes. Finally, the design of the system may be scaled down to a mobile, lightweight unit.

Moreover, at bulk-hydrogen production scales, a multi-tubular (multiple distributed

15   combustion tubes and/or multiple hydrogen selective and permeable membrane tubes) containing reactor disclosed herein provides the modularity needed. A producer can match the desired capacity by installing multiple reactor units of the specific design or having multiple distributed combustion tubes and/or multiple hydrogen selective and permeable membrane units in a large steam reformer. This is more cost-effective than either trying to scale

20   up or down the existing large box furnace reactor designs or building several thousand single-tube reactors.

The hydrogen-producing reactor of the present invention comprises a) reaction chamber comprising:(i) an inlet adapted to receive a hydrogen-producing feedstock, and (ii) a catalyst bed for producing reaction products comprising hydrogen gas from the hydrogen-

25   producing feedstock; and b) at least one hydrogen selective, hydrogen permeable composite gas separation module adapted to receive the reaction products from the catalyst bed and to separate the reaction products into (1) a product stream comprising a major amount of hydrogen and (2) a by-product stream; wherein the composite gas separation module comprises: (i) a porous substrate; (ii) an intermediate porous metal, wherein the intermediate

30   metal layer overlies the porous metal substrate; and (iii) a dense gas-selective membrane, wherein the dense gas-selective membrane overlies the intermediate layer.

Non-limiting illustrative example of the hydrogen-producing feedstock include natural gas, methane, ethyl benzene, methanol, ethane, ethanol, propane, butane, light hy-

drocarbons having 1-4 carbon atoms in each molecule, light petroleum fractions including

naphtha, diesel, kerosene, jet fuel or gas oil, and hydrogen, carbon monoxide and mixtures

thereof.

In a particular embodiment, the catalyst bed contains baffles in a form selected

from the group consisting of (i) washers and disks, and (ii) truncated disks.

In a particular embodiment, the reactor is suitable for a dehydrogenation reaction

and has a dehydrogenation chamber containing a dehydrogenation catalyst bed with a de-

hydrogenation catalyst such as an iron-oxdide-containing catalyst. The invention also re-

lates to a process for the dehydrogenation of ethylbenzene comprising the steps of feeding

ethylbenzene into the reactor as described above to produce styrene and hydrogen.

The reactor can be a steam-reforming reactor wherein the reaction chamber is a

steam reforming reaction chamber comprising a catalyst bed comprising a steam reforming

catalyst. In another embodiment, the present invention also relates to a steam reforming

process comprising the steps of reacting a hydrogen-producing feedstock and steam in a

reactor as described above. The steam reforming process for the production of hydrogen

can comprise the steps of a) reacting steam with a hydrogen-producing feedstock at a tem-

perature of from about 200°C to about 700°C and at a pressure of from about 1 bara (abso-

lute)(0.1 MPa (absolute)) to about 200 bara (absolute)(20 MPa (absolute)) in a steam re-

forming reaction chamber containing a reforming catalyst to produce a mixture of primar-

ily hydrogen and carbon dioxide, with a lesser amount of carbon monoxide; and b) con-

ducting said reaction in the vicinity of at least one hydrogen-permeable, hydrogen-selective

membrane tube, whereby hydrogen formed in said reaction zone permeates through said

hydrogen selective membrane tube and is separated from said carbon dioxide and carbon

monoxide; wherein the hydrogen selective, hydrogen permeable membrane tube is made of

a composite gas separation module as described herein. In a particular embodiment, the

carbon dioxide produced from said steam reforming chamber may have a pressure of from

about 0.1 to about 20 MPa, particularly from about 1 to about 5 MPa and the carbon diox-

ide produced from the steam reforming chamber has a concentration of from about 80% to

about 99% molar dry basis, or of from about 90% to about 95% molar dry basis. In a par-

ticular embodiment, the carbon dioxide produced from the steam reforming chamber is

used at least in part for enhanced recovery of oil in oil wells or enhanced recovery of meth-

ane in coal bed methane formations.

In some embodiments, the afore-mentioned hydrogen-producing reactors, including the steam reformer and dehydrogenation reactor, further comprises at least one heater comprising a distributed combustion chamber in a heat transferring relationship with the catalyst bed. The distributed combustion chamber comprises an inlet and a flow path for an oxidant, an outlet for combustion gas, and a fuel conduit having an inlet for fuel and a plurality of fuel nozzles or openings which provide fluid communication from within the fuel conduit to the flow path of said oxidant. The plurality of fuel nozzles or openings are sized and spaced along the length of said fuel conduit to avoid hot spot formation when the fuel is mixed with said oxidant in said distributed combustion chamber. In one embodiment, the distributed combustion does not form any flame when the fuel is mixed with said oxidant in said distributed combustion chamber and during its heating operation. The distributed combustion heater(s) may also have a preheater capable of preheating the oxidant, such as air or oxygen, to a temperature that when said fuel and said oxidant are mixed in the distributed combustion chamber, the temperature of the resulting mixture of said oxidant and fuel exceeds the autoignition temperature of said mixture. In some other embodiments, the ratio of the surface area of said distributed combustion chambers to the surface area of said membrane tubes is from about 0.1 to about 20.0, particularly from about 0.2 to about 5.0, more particularly from about 0.5 to about 5.0, and still more particularly from about 0.3 to about 3.0 and even more particularly from about 1.0 to about 3.0. In still some other embodiments, the distributed combustion chamber may have an external tubular dimension such that the length to diameter ratio is higher than 4, or higher than 10

As a particular embodiment, the hydrogen-selective, hydrogen-permeable composite gas separation module is connected to a section containing a metal hydride precursor, and the hydrogen formed in the reforming chamber permeates through the membrane tube to the section containing the metal hydride precursor which reacts with the permeated hydrogen to form hydride. This reaction reduces the effective partial pressure of hydrogen in the permeate stream and drives the equilibrium within the reaction chamber to produce more hydrogen from the feedstock.

In some embodiments, the reactor may contain multiple distributed combustion chambers and/or multiple hydrogen separation tubes. In some embodiments, the products produced are separated by hydrogen-selective, hydrogen-permeable hydrogen separation membrane tube(s) having a ratio of length to diameter of less than about 500, wherein gaps between the membrane tubes are from about ¼ inch (about 0.64 cm) to about 2 inches

(about 5.08 cm), and wherein gaps between the membrane and distributed combustion ("DC") tubes are from about ¼ inch (about 0.64 cm) to about 2 inches (about 5.08 cm); or the hydrogen-selective and hydrogen-permeable membrane tube(s) have a ratio of length to diameter of less than about 250, wherein gaps between the membrane tubes are from about

5 ½ inch (about 1.27 cm) to about 1 inch (about 2.54 cm), and gaps between the membrane and DC tubes are from about ½ inch (about 1.27 cm) to about 1 inch (about 2.54 cm).

In some embodiments, a sweep gas is used to promote the diffusion of hydrogen through the hydrogen separation module. The sweep gas can be, but is not limited to, steam, carbon dioxide, nitrogen and condensable hydrocarbon.

10   In some embodiments, the hydrogen-selective membrane is palladium or an alloy thereof and the porous substrate is a porous metal substrate or a porous ceramic substrate. Non-limiting illustrative examples of the palladium alloy include alloys of palladium with least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium. Illustrative non-limiting examples of the

15 porous metal substrate include (i) stainless steel, (ii) an alloy comprising chromium and nickel, (iii) a nickel-based alloy, (iv) an alloy comprising chromium, nickel and molybdenum, (v) porous Hastelloy®, and (vi) porous Inconel.

In one embodiment, the intermediate layer comprises palladium or palladium and a Group IB metal. In a particular embodiment, the Group IB metal is silver or copper. In an-

20 other particular embodiment, the intermediate porous metal layer comprises alternating layers of palladium and the Group IB metal. In some embodiments, the thickness of the intermediate porous metal layer is selected from the group consisting of (i) at least about 5 micrometers thick, (ii) about 1 to about 10 micrometers thick, and (iii) about 4 to about 8 micrometers.

25   In one embodiment, the mean pore size of the intermediate porous metal layer is less than the mean pore size of the porous metal substrate. In some embodiments, the composite gas separation module further comprises one or more of the following features: (i) a layer of a ceramic bonded to the porous metal substrate and underlying the intermediate porous metal layer, (ii) the surface of the porous metal substrate being oxidized prior to

30 applying the intermediate porous metal layer, and/or (iii) the porous metal substrate being activated, such as seeded with nuclei of a hydrogen-selective metal prior to applying the intermediate porous metal layer.

In a particular embodiment, the surface of the intermediate porous metal layer is abraded to form a polished substrate, prior to application of the dense hydrogen-selective membrane over the intermediate porous metal layer. In another particular embodiment, the composite gas separation module is made by a step of depositing a hydrogen-selective

5   metal on the intermediate porous metal layer, thereby forming a coated substrate and abrading the surface of the coated substrate, thereby forming an polished substrate, prior to application of the dense hydrogen-selective membrane over the intermediate porous metal layer.

In some embodiments, the hydrogen flux through the module is at least about 4

10   Nm^3/m^2-hr, particularly at least about 10 Nm^3/m^2-hr, and more particularly at least about 28 Nm^3/m^2-hr at about 350°C and with a hydrogen partial pressure difference of about 1 bara (absolute) (0.1 MPa (absolute)) in the permeate side and 2 bara (absolute)(0.2 MPa (absolute)) in the process side.

In one embodiment, the present invention relates to a distributed combustion

15   heated, membrane, dehydrogenation reactor comprising:

a)   a dehydrogenation chamber containing a catalyst bed, said dehydrogenation chamber having an inlet for vaporizable hydrocarbon, a flow path for hydrogen and product gases resulting from the dehydrogenation reactions taking place in said dehydrogenation chamber and an outlet for said product

20   gases,

b)   at least one distributed combustion chamber in a heat transferring relationship with said catalyst bed whereby a distributed, controlled heat flux is provided by said distributed combustion chamber to said catalyst bed, said distributed combustion chamber comprising an inlet and a flow path for an

25   oxidant, an outlet for combustion gas and further comprising a fuel conduit having an inlet for fuel and a plurality of fuel nozzles which provide fluid communication from within the fuel conduit to the flow path of said oxidant, said plurality of fuel nozzles being sized and spaced along the length of said fuel conduit so that no flame results when said fuel is mixed with

30   said oxidant in said distributed combustion chamber;

c)   a preheater capable of preheating said oxidant to a temperature that when said fuel and said oxidant are mixed in said distributed combustion cham-

ber, the temperature of the resulting mixture of said oxidant and fuel exceeds the autoignition temperature of said mixture; and

d)   at least one hydrogen-selective, hydrogen-permeable, membrane tube in contact with said catalyst bed, said membrane tube having an outlet whereby hydrogen formed in the dehydrogenation chamber permeates into said membrane tube and passes through said outlet.

In the present invention, heat transfer limitations are overcome by the innovative use of distributed combustion (distributed combustion) as the primary heat source. Distributed combustion is used to distribute heat throughout the reactor at high heat fluxes without high temperature flames and with low NOx production. This is achieved by injecting small quantities of fuel into a preheated air stream and reaching autoignition conditions. Fuel quantity is controlled by nozzle size, the temperature rise is very small, and there is much reduced or substantially no hot spots such as flame associated with the combustion (combustion is kinetically limited, rather than mass-transfer limited).

Distributed combustion is disclosed in U.S. 5,255,742, U.S. 5,862,858, U.S. 5,899,269, U.S. 6,019,172, and EP 1 021 682 B1.

An important feature of the distributed combustion is that heat is removed along the length of the combustion chamber so that a temperature is maintained that is significantly below what an adiabatic combustion temperature would be. This almost eliminates formation of NOx, and also significantly reduces metallurgical requirements, thus permitting the use of less expensive materials in construction of equipment.

Generally, distributed combustion involves employing a fuel conduit having an inlet for fuel and a plurality of fuel nozzles or openings which provide fluid communication from within the fuel conduit to the flow path of said oxidant. The plurality of fuel nozzles or openings are sized and spaced along the length of said fuel conduit to avoid hot spot formation when the fuel is mixed with said oxidant in said distributed combustion chamber. It also involves preheating combustion air and fuel gas (e.g., methane, methanol, hydrogen and the like) sufficiently such that when the two streams are combined the temperature of the mixture exceeds the autoignition temperature of the mixture, but to a temperature less than that which would result in the oxidation upon mixing, being limited by the rate of mixing. Preheating of the combustion air and fuel streams to a temperature between about 1500°F (about 815°C) and about 2300°F (1260°C) and then mixing the streams in relatively small increments will result in distributed combustion to avoid hot spots, such as

flames. For some fuels such as methanol, preheating to a temperature above about 1000°F (about 537°C) is sufficient. The increments in which the fuel gas is mixed with the combustion gas stream preferably result in about a 20° to about 200°F (or 11 to 110°C) temperature rise in the combustion gas stream due to the combustion of the fuel.

5   With most hydrogen-producing, such as steam methane reforming, processes controlling the temperature in the catalyst bed is a problem. The advantages of the distributed combustion as a heat source in the present process and apparatus can be summarized as follows:

- DC helps maintain a more uniform temperature, but simultaneously controls heat flux
10   to match the local heat needed for the material left to be reacted.   At the highest heat flux there is as much heat present as can be accommodated by the reaction and as the process progresses less and less heat is required to drive the reaction.

- DC has a lower maximum-temperature combustion gas.

- DC does not have hot spots which might damage the hydrogen-selective, hydrogen-
15   permeable membrane.

- DC has a negligible NO_x production.

- DC makes it easier to tailor axial heat flux distribution to minimize entropy production or energy loss and, thus, making it more efficient.

- DC permits a more compact reactor design that is less expensive to build.

20 • DC permits a modular reactor design, at a wide range of sizes and heat duties.

- DC provides a tapered heat flux profile.

Thus, the distributed combustion (DC) used to drive the steam reforming reactions in the present invention can be described as comprising:

a)   preheating either a fuel gas or oxidant or both to a temperature that exceeds the
25   autoignition temperature of the mixture of the fuel gas and oxidant when they are mixed;

b)   passing said fuel gas and oxidant into a heating zone which is in heat transferring contact along a substantial portion of the reaction zone (i.e., the zone in which said reforming reactions take place); and

30   c)   mixing the fuel gas and oxidant in said heating zone in a manner that autoignition occurs, resulting in combustion without high temperature hot spots such as flames, thereby providing uniform, controllable heat to said reaction zone.
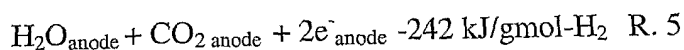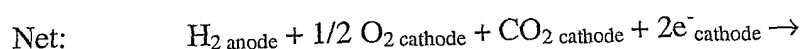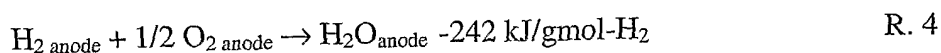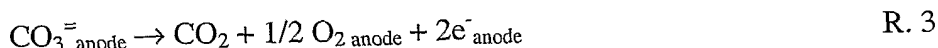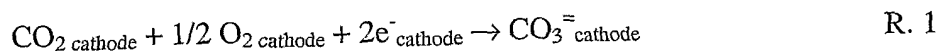
In the practice of the invention, some degree of sulfur removal will probably be necessary to protect the palladium material making up the hydrogen-permeable separation membrane and the Ni reforming catalyst. Sulfur is a temporary poison to such catalysts, but the catalyst activity can be regenerated by removing the source of sulfur. The sulfur

5   tolerance of commercial reforming catalysts is dependent upon process conditions. On average, sulfur must be reduced to below 10 ppb to allow the catalyst to function properly.

Feed clean up with ZnO beds or by other means known in the art may be used to remove impurities such as H_2S and other sulfur containing compounds in the feed that could contribute to membrane degradation. For heavier hydrocarbons, like naphtha, some

10   hydrotreating may be necessary to convert organic sulfur to H_2S, as known in the art. Heavy oil, solids carried by liquid water, oxygen, amines, halides, and ammonia are also known poisons for palladium membranes. Carbon monoxide competes with hydrogen for active surface sites, thus reducing the hydrogen permeability by 10% at 3-5 Bar (0.3-0.5 MPa). Thus, the partial pressure needs to stay low for best performance, as is the case in

15   our preferred design.

In another embodiment of the present invention the pure hydrogen generated by the present reactor and process is used in an integrated design to power a fuel cell such as high pressure molten carbonate fuel cell, PEM (proton exchange membrane) fuel cells or SOFC (solid oxide fuel cells) and the like. This embodiment of the present invention has the po-

20   tential for about 71% or greater efficiency in the generation of electricity from starting fuel. In addition, due to the unique integration of the system, CO_2 is produced in high concentrations from about 80% to about 95% molar dry basis, and high pressure of from about 0.1 to about 20 MPa, particularly from about 1 to about 5 MPa, and is easier to separate from nitrogen, which makes the system even more efficient.

25   Referring now to Figure 14, a hydrogen-producing feedstock such as vaporizable hydrocarbon and steam 5 are fed into the catalyst section 4 of a DC-membrane reactor of the type described in Figure 1, while preheated air 7 and fuel 14 are fed into the DC heating section 2 of the reactor containing fuel tubes 10. A sweep gas (in this case steam) is fed into the DC-membrane reactor at 6. The produced high purity hydrogen stream, 12, is di-

30   rected to the anode compartment of the molten carbonate fuel cell, 20, operating at about 650 °C and 5 Bar (0.5 MPa). The reactor effluent 13 containing the unreacted steam, CO_2 and low quantities of methane, hydrogen and CO, and the flue gas 11 from the DC heater and air, 16 are fed to the cathode compartment of the same fuel cell, 17. The CO_2 reacts

with the O_2 to form $CO_3^=$ anions that transport through the molten carbonate membrane. The $CO_3^=$ anions are constantly renewed. The reactions with indicated transport are described as follows:

$$CO_{2\ cathode} + 1/2\ O_{2\ cathode} + 2e^-_{cathode} \rightarrow CO_3^={}_{cathode} \qquad \text{R. 1}$$

$$CO_3^={}_{cathode} \rightarrow CO_3^={}_{anode} \qquad \text{R. 2}$$

$$CO_3^={}_{anode} \rightarrow CO_2 + 1/2\ O_{2\ anode} + 2e^-_{anode} \qquad \text{R. 3}$$

$$H_{2\ anode} + 1/2\ O_{2\ anode} \rightarrow H_2O_{anode}\ -242\ kJ/gmol\text{-}H_2 \qquad \text{R. 4}$$

Net: $H_{2\ anode} + 1/2\ O_{2\ cathode} + CO_{2\ cathode} + 2e^-_{cathode} \rightarrow$

$$H_2O_{anode} + CO_{2\ anode} + 2e^-_{anode}\ -242\ kJ/gmol\text{-}H_2 \quad \text{R. 5}$$

Electricity generated by the fuel cell is shown as electrical output **21**. The stream from the anode, **22**, now contains the permeated CO_2 and steam but no hydrogen, nitrogen, methane or oxygen, if hydrogen and oxygen are fed in exactly 2:1 stoichiometry. A portion of stream **22** may recycled to the cathode compartment **17** of the fuel cell. The CO_2 recycle stream is shown as **23** on Figure 6. A portion of streams **22** and/or **13** also may be put through a turbine expander to generate electrical or mechanical work **30** and **24**, respectively. In the present invention CO_2 is separated from nitrogen essentially for free while electricity is simultaneously generated. Furthermore the CO_2 capture leverage is high. As shown above, each mole of methane is converted to 4 moles of H_2. Therefore 4 moles of CO_2 per mole of converted methane are required to transport the oxygen in the fuel cell and are therefore separated from the nitrogen. Thus, this process can also be used to separate CO_2 from an external CO_2 containing stream. The high concentration CO_2 stream, **29**, is now a prime candidate for sequestration after the steam is condensed. The CO_2 can be used for oil recovery, or injected into subterranean formations, or converted to a thermodynamically stable solid. Also, since the present process can be operated to produce high purity hydrogen and nitrogen as well as concentrated CO_2, it can be used to facilitate the production of chemicals such as urea, which can be made from these three raw materials. Other chemicals which can be manufactured using the products and by-products of the present process include ammomia and ammonium sulfate. Other uses for the con-

centrated stream of CO_2 and the high purity hydrogen and nitrogen streams will be apparent to those skilled in the art.

The stream from the cathode, stream 18, contains all the nitrogen, unreacted oxygen, a little unpermeated CO_2, and trace amounts of the methane, hydrogen and CO from the MSR effluent. All or part of this stream can be put through a turbine expander (not shown) to generate work (electrical or mechanical), 19. The trace components of stream 18 may be oxidized in a catalytic converter, 26, and emitted in the atmosphere as a low CO_2 concentration containing stream, 27, containing less than 10% CO_2, preferably less than 1% CO_2. The trace components may also be oxidized inside the fuel cell if the appropriate catalyst is placed in the cathode compartment. A stream, 28, containing water and steam exits condenser 25 and is recycled to the DC-MSR reactor, and reheated to between about 250 to 500°C.

The zero emission hybrid system of the present invention is extremely efficient. Byproduct compounds are separated, the steam and hydrogen are reheated efficiently, and electricity is produced. Furthermore, water is separated from purified CO_2 which is produced in concentrations large enough to be easily sequestered. Advantages include using waste heat to raise steam and using water collected for recycling to support additional steam reforming or other beneficial uses. The system is a totally integrated, extremely efficient design having the potential for greater than 71% generation efficiency as mentioned above. The 71% is approximately a 20% fractional improvement over the best results we are aware of in the art, the 60% figure mentioned above that is possible under laboratory conditions. In addition to the great improvement in efficiency, the integrated design provides a concentrated source of CO_2 for capture and sequestration as well.

Fuel cells which would be suitable for use in the present invention are those that could function in a highly pressurized system. Most fuel cells run at atmospheric conditions. For this reason, a high pressure molten carbonate fuel cell is preferred. However, other types of fuel cells, such as PEM fuel cells and SOFC, can also be effectively combined with the DC-MSR reactor of the present invention.

Another very attractive feature is that the DC powered MSR hydrogen generator produces very low NO_x, especially compared with the combined processes known in the art. Due to the use of distributed combustion very little NO_x is generated in this system. Furthermore, other steam reforming reactors used to generate hydrogen known in the art

could not feed to the MCFC the flue gas from the furnace as in the present design, because
they produce high NO_x, which would poison the molten carbonate membrane.

In a particular embodiment of the invention, the aforesaid distributed combustion
heated, membrane hydrogen-producing reactor such as a steam reforming reactor contains

5   multiple distributed combustion chambers (preferably, but not necessarily, in the form of
tubes) and multiple hydrogen-selective, hydrogen-permeable membrane tubes disposed in,
or otherwise in contact with, the reforming catalyst bed in the reforming chamber. Exam-
ples of multi-tubular reactors in accordance with the invention are shown in Figures 4-5, 7-
8 and 10-13.

10   The multi-tubular, distributed combustion heated, membrane hydrogen-producing
reactor such as steam reforming reactor in accordance with the invention may be either of
the radial flow type as shown in Figures 4 and 5, or may be of the axial flow type as shown
in Figures 7-8 and 12-13. In a radial flow reactor the gases generally flow through the re-
forming catalyst bed radially from outside to inside (or from inside to outside), while in an

15   axial flow reactor the gases generally flow through the reforming catalyst bed in the same
direction as the axis of the reactor. In the case of a vertical reactor, the flow would be from
the top of the reactor to the bottom, or the bottom of the reactor to the top.

The multi-tubular, distributed combustion heated, membrane reactor such as a
steam reforming reactor in accordance with the present invention may contain from as few

20   as 2 distributed combustion tubes up to 100 or more, particularly 3 to 19, depending the
size of the distributed combustion tubes, the size of the catalyst bed and the level of heat
flux desired in the catalyst bed. The size of the distributed combustion tubes can vary from
about 1 inch (2.5 cm) outer diameter up to about 40 inches (102 cm) or more outer diame-
ter. The number of hydrogen-selective membrane tubes may also vary from as few as 2 up

25   to 400 or more, particularly 3 to 90. The size of the membrane tubes may vary from about
1 inch (2.5 cm) outer diameter up to about 10 inches (25 cm) outer diameter or more. In
general, the ratio of distributed combustion tube surface area to membrane tube surface
area will be in the range of about 0.1 to about 20.0, particularly from about 0.2 to about
5.0, more particularly from about 0.5 to about 5.0, still more particularly from about 0.3 to

30   about 3.0 and even more particularly from about 1.0 to about 3.0. The term "surface area"
when used in reference to the above ratios, means the external (circumferential) area of the
distributed combustion tubes and the membrane tubes. For instance, a 1 inch (2.5 cm)

outer diameter tube of 12 inches (30 cm) length would have an external surface area of 37.6 square inches.

Each distributed combustion tube or chamber will have at least one fuel conduit disposed therein. Large distributed combustion chambers generally will have multiple fuel
5   conduits. The distributed combustion chambers or tubes employed in the multi-tubular reactors of the invention may be "open ended" or "closed ended" as discussed below in connection with Figures 6A and 6B.

A sweep gas may be used to promote the diffusion of hydrogen through the hydrogen-selective, hydrogen-permeable membrane. In case a sweep gas is employed, the membrane
10   brane tube may contain an inlet and flow path for sweep gas feed and a flow path and outlet for the return of sweep gas and permeated hydrogen.

Baffles and/or screens may also be employed in the multi-tubular reactors of the present invention to improve contact of the reactive gases with the catalyst and to improve flow distribution. The distributed combustion tubes and/or membrane tubes may also be
15   surrounded by cylindrical screens to protect the tubes from direct contact with the catalyst.

In one embodiment, the present reactor is an integrated distributed combustion-steam reformer, and the present process or apparatus of is capable of producing high purity hydrogen with minimal production of CO, particularly less than about 5 molar%, more particularly less than 3 molar %, and still more particularly less than 2 molar% on a molar dry
20   basis of the total products, and with less than 1000 ppm of CO and particularly less than 10 ppm of CO on a dry basis, more particularly virtually no CO in the hydrogen stream produced. By practice of the present invention it is possible to produce high purity hydrogen e.g., hydrogen having a purity on a dry basis of greater than 95%. The present invention can be used to produce hydrogen having purities as high as 97%, 99%, or under optimum
25   conditions 99+%. The effluent (by product) stream from the MSR reactor will typically contain more than 80% CO_2 on a dry basis, e.g., 90% CO_2, 95% CO_2 or 99% CO_2, and less than about 10% CO on a dry basis, e.g., less than about 5% CO, preferably less than 1% CO.

Total heat management and turbines may be included in the system to increase the
30   efficiency and produce additional electricity or to do useful work such as compress gases or vapors.

One aspect of the present invention is a distributed combustion heated membrane steam reformer hydrogen generator. In the design of the invention there are disclosed dis-

tinct improvements in overall efficiency, particularly size, scalability and heat exchange. The present invention typically employs only one reactor to produce the hydrogen versus typically four reactors used in conventional processes, and part of the heat load is supplied by the water-gas-shift reaction. The design of the invention captures essentially all of the

5   heat in the reaction chamber since heat exchange occurs on a molecular level, which reduces the overall energy requirements.

Chemical equilibrium and heat transfer limitations are the two factors that govern the production of hydrogen from hydrogen-producing feedstock in conventional reactors. These factors lead to the construction of large reactors fabricated from expensive high

10   temperature tolerant materials. They are enclosed in high temperature furnaces that are needed to supply the high heat fluxes.

In the present invention the two major limitations of chemical equilibrium and heat transfer are overcome by the innovative combination of an in-situ membrane separation of hydrogen in combination with a heat source comprising distributed combustion ("DC")

15   that makes it possible to more efficiently use all the energy in the system, as well as provide load following capabilities.

The reformer of the present invention reduces the operating temperature of the steam reforming reactor close to the lower temperature used in a shift reactor. With the temperatures for the steam reforming and shift closer, both operations are combined into

20   one reactor. With both reactions occurring in the same reactor the exothermic heat of reaction of the shift reaction is completely captured to drive the endothermic steam reforming reaction. This reduces the total energy input for the sum of the reactions by 20%. The lower temperature reduces stress and corrosion and allows the reactor to be constructed from much less expensive materials. Combining the operations also reduces the capital

25   and operating cost since only one reactor, instead of two or three, are required. Moreover, the reaction is not kinetics-limited even at the lower temperature, thus, the same or even less catalyst can be used.

The general description for steam reformers, including but not limited to the reactions, enthalpies, values of equilibrium constants, advantages of integrated distributed

30   combustion-SMR reactor, as well as the advantages of the use of the membrane in the reactor can be found in US 2003/0068269.

The in-situ membrane separation of hydrogen employs a membrane fabricated, particularly from an appropriate metal or metal alloy, on a porous ceramic or porous metal

support, as described below, to drive the equilibrium to high conversions. With constant

removal of the hydrogen through the membrane, the reactor can be run at much lower than

the commercially practiced temperatures of 700-900+°C. A temperature of 500°C is suffi-

cient to drive the kinetics to high conversions when the equilibrium is shifted using the hy-

5   drogen separation membrane. At this temperature the selectivity to CO_2 is almost 100%,

while higher temperatures favor the formation of CO as a major product.

The term "reforming catalyst" as used herein means any catalyst suitable for cata-

lyzing a steam reforming reaction, which includes any steam reforming catalyst known to

one skilled in the art, as well as any "pre-reforming catalyst" which is suitable for catalyz-

10   ing steam reforming reactions in addition to being suitable for processing heavier hydro-

carbons prior to a steam reforming reaction.

Figure 1 shows a schematic diagram of a hydrogen-producing reactor with catalyst

section, and permeate section. The reactor 1 shown in Figure 1 consists of two concentric

sections. The inner concentric section 3 is the permeate section. The annulus, 4, in be-

15   tween is the catalyst section. A hydrogen-producing catalyst, such as a reforming catalyst,

is loaded into the annulus section 4 wherein the above-described reactions take place. (sec-

tion 4 is also variously referred as the catalyst section, the reaction section or the reaction

zone). The membrane, 8, is represented on the inside of the small section, 3, (the permeate

section) in Figure 1.

20   The feed stream containing hydrogen-producing feedstock, such as a mixture of

vaporizable hydrocarbon-containing compounds (e.g. naphtha, methane or methanol) and

H_2O with a minimum overall O: C ratio of 2:1 when a steam reforming reaction is carried

out, enters catalyst section 4 at 5. If used, sweep gas for promoting the diffusion of hydro-

gen through the membrane enters the top of the permeate section 3 at 6. Alternatively,

25   sweep gas can be introduced into the permeate section by means of a stinger pipe fitted to

bottom of the permeate section. In case of this alternative, hydrogen in sweep gas would

exit the permeate zone at the bottom of the permeate section. Optionally, the stinger pipe

to introduce the sweep gas may be connected at the top of the permeate section in which

case the hydrogen and sweep gas would exit at the top of this section. Hydrogen (pure or

30   in sweep gas) exits at 12. Unreacted products and by-products (e.g., CO_2, H_2O, H_2, CH_4,

and CO) exit catalyst section 4 at 13. It is also possible to remove the produced hydrogen

using a vacuum instead of a sweep gas.

The catalyst beds, 4, can be heated by any suitable heating method known to one skilled in the art, such as a by a traditional burner, an electric heating means, a microwave heating means, etc.

Any hydrogen-producing, particularly vaporizable, feedstock such as an (optionally

5   oxygenated) hydrocarbon-containing compound(s) can be used in the present process and apparatus, including, but not limited to, methane, methanol, ethane, ethanol, propane, butane, light hydrocarbons having 1-4 carbon atoms in each molecule, and light petroleum fractions like naphtha at boiling point range of 120-400°F, which is a typical feed for commercial steam reformers. Petroleum fractions heavier than naphtha can also be em-

10 ployed like diesel or kerosene or jet fuel at boiling point range of 350-500°F or gas oil at boiling point range of 450-800°F. Hydrogen, carbon monoxide and mixtures thereof, e.g., syn gas, may also be used in the process and apparatus of the present invention, and are included in the definition of "hydrogen-producing feedstock" or "vaporizable hydrocarbon". Methane was used in the examples to demonstrate the process. The catalyst bed can

15 be heated 107 by any suitable means 107, such as electric heating, microwave, conventional combustion, distributed combustion, etc.

In some embodiments, with the distributed combustion-steam reforming process and apparatus of the present invention it is possible to use O: C ratios as low as 2.8, down to 2.6, without coking problems, with the minimum O: C ratio being about 2:1. This re-

20 sults lower energy costs if methane is used as the feed in the present invention, since lower steam to methane ratios can be used thus requiring less energy to vaporize water. Because of the ability to operate at lower O:C ratios, it is also possible to use heavier, less expensive feeds in the distributed combustion-MSR reactor of the present invention than can be used in conventional steam methane reformers.

25 In another embodiment of the invention, the integrated hydrogen-producing process and apparatus of the invention can be used to perform water-gas-shift reactions on syngas mixtures (i.e., mixtures of hydrogen and carbon monoxide) produced from conventional processes like Catalytic Partial Oxidation (CPO), Steam Methane Reforming (SMR) and Autothermal Reforming (ATR). The integrated distributed combustion-MSR reactor is

30 well suited for this since it produces high purity hydrogen and converts carbon monoxide to carbon dioxide and more hydrogen. Thus, the versatile hydrogen-producing reactor of the invention is capable of replacing the high temperature shift, low temperature shift and methanation reactors and the hydrogen purification section. A mixture of syngas and va-

porizable hydrocarbon can also be used to yield a net reaction which may be either endo-thermic, thermally neutral or slightly exothermic.

The reactor annulus is packed with steam reforming catalyst and equipped with a perm-selective (i.e., hydrogen selective) membrane that separates hydrogen from the re-

5   maining gases as they pass through the catalyst bed. The steam reforming catalyst can be any known in the art. Typically steam reforming catalysts which can be used include, but are not limited to, Group VIII transition metals, particularly nickel. It is often desirable to support the reforming catalysts on a refractory substrate (or support). The support is pref-erably an inert compound. Suitable compounds contain elements of Group III and IV of

10   the Periodic Table, such as, for example the oxides or carbides of Al, Si, Ti, Mg, Ce and Zr. The preferred support composition for the reforming catalyst is alumina.

The catalyst used in the examples to demonstrate the present invention was nickel on porous alumina. As the hydrogen is formed in the catalyst bed, it is transported out through the hydrogen-permeable separation membrane filter. Advantages of this technol-

15   ogy include the capacity to separate essentially pure hydrogen from any poisons that may also be present, including CO and H_2S, and from other fuel diluents. The poisons do not pass through the separation membrane, which is fabricated from one of a variety of hydro-gen-permeable and hydrogen–selective materials including ceramics.

The composite gas separation modules described herein include a dense gas-

20   selective membrane such as, for example, a dense hydrogen-selective membrane. The dense hydrogen-selective membrane can include, for example, palladium or an alloy thereof. A "dense gas-selective membrane," as that term is used herein, refers to a compo-nent of a composite gas separation module that has one or more layers of a gas-selective material, i.e., a material that is selectively permeable to a gas, and that is not materially

25   breached by regions or points which impair the separation of the gas by allowing the pas-sage of an undesired gas. For instance, in one embodiment, the dense gas-selective mem-brane is not materially breached by regions or points which do not have the desired gas se-lectivity properties of the gas-selective material. An example of a dense gas-selective membrane is a dense hydrogen-selective membrane that is substantially free of defects

30   such as open pores, holes, cracks and other physical conditions that impair the gas-selectivity of the composite gas separation module by allowing the passage of an undesired gas. In some embodiments, a dense gas-separation membrane can contain one or more non-metallic components, however, the dense gas-separation membranes described herein

20

contain at least one metallic component (*e.g.*, a hydrogen-selective metal such as palladium or an alloy thereof).

The term "support," as used herein, includes a substrate, a surface treated substrate, a substrate upon which a material (*e.g.*, a gas-selective material) has been deposited, a sub-
5   strate with an overlying intermediate porous metal layer, or a subsequently plated substrate upon which a dense gas-selective membrane has been or will be formed. Serving as a support structure, the substrate can enhance the durability and strength of the composite gas separation module.

"Gas-selective material," as used herein, refers to those materials which, when
10   formed into dense gas-selective membranes, allow the passage of a select gas, or select gases, through the dense gas-selective membrane. Suitable gas-selective materials include metals, ceramics (*e.g.*, perovskite and perovskite-like materials) and zeolites (*e.g.*, MFI and Zeolites A, X, etc.). In one embodiment, the gas-selective material is a hydrogen-selective metal such as palladium or an alloy thereof. Examples of suitable palladium alloys include
15   palladium alloyed with at least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium. For example, palladium/silver and palladium/copper alloys can be used to form dense hydrogen-selective membranes. In one embodiment, the gas-selective material is a ceramic such as oxygen gas-selective perovskite.

20   The side of the support upon which the dense gas-selective membrane is formed is referred to herein as the "outside" or "membrane-side" and the opposite side of the support is called the "inside" or "substrate-side" surface. However, it should be noted that the dense gas-selective membrane can be formed on the exterior surface and/or the interior surface of the substrate. For example, the dense gas-selective membrane can be formed on
25   either or both surfaces of a planar substrate or can be formed on the exterior and/or interior surfaces of a substrate tube. Preferably, the dense gas-selective membrane is formed on only one surface of the substrate, for example, on either the exterior or the interior surface of a substrate tube.

In one embodiment, the gas-selective material can include a combination of sub-
30   stances, for example, a combination of a hydrogen-selective metal and a zeolite. In one embodiment, the zeolite used in a combination of substances is gas-selective. In an alternative embodiment, the zeolite used in a combination of substances is not gas-selective, for example, the zeolite used in a combination of substances is not hydrogen-selective.

Figure 2 illustrates a cylindrical composite gas separation module 110 as one em-
bodiment of the invention. Composite gas separation module 110 includes porous sub-
strate 112, intermediate porous metal layer 114, and dense gas-selective membrane 116.
As illustrated, intermediate porous metal layer 114 and dense gas-selective membrane 116

5   overlie the outside surface of cylindrical porous substrate 112. In alternative embodiments
not illustrated, intermediate porous metal layer 114 and dense gas-selective membrane 116
can overlie the interior surface of cylindrical porous substrate 112 (with the dense gas-
selective membrane forming the innermost of the three cylindrical layers) or can overlie
both the interior and the exterior surfaces of porous substrate 112. In a preferred embodi-

10   ment, intermediate porous metal layer 114 and dense gas-selective membrane 116 overlie
only either the interior or the exterior surface of porous substrate 112. The composite gas
separation module can take any of a variety of forms including a cylindrical tube, as illus-
trated in Figure 2, or a planar surface. In one embodiment, porous metal substrate 112 also
includes a layer of ceramic bonded thereto.

15   The composite gas separation module used herein includes a porous metal sub-
strate. The porous metal substrate can be formed from any of a variety of components
known to those of ordinary skill in the art. Examples of suitable substrate components in-
clude, but are not limited to, iron, nickel, palladium, platinum, titanium, chromium, porous
silver, porous copper, aluminum, and alloys thereof, e.g., steel, stainless steel, porous

20   stainless steel, HASTELLOY® alloys (e.g., HASTELLOY® C-22®) (trademarks of Haynes
International, Inc., Kokomo, IN) and INCONEL® alloys (e.g., INCONEL® alloy 625) (IN-
CONEL is a trademark of Huntington Alloys Corp., Huntington WV). In one embodiment,
the porous metal substrate is an alloy containing chromium and nickel (e.g., INCONEL®
alloy 625). In an additional embodiment, the alloy contains chromium, nickel and molyb-

25   denum such as, for example, HASTELLOY® C-22® or INCONEL® alloy 625. The porous
metal substrate can be porous stainless steel. Cylinders of porous stainless steel that are
suitable for use as substrates are available from Mott Metallurgical Corporation (Farming-
ton, CT) and from Pall Corporation (East Hills, NY), for example. The substrate can also
be metal mesh, sintered metal powder, refractory metals, metal oxides, ceramics, porous

30   refractory solids, honeycomb alumina, aluminate, silica, porous plates, zirconia, cordierite,
mullite, magnesia, silica matrix, silica alumina, porous Vycar, carbon, glasses, and the like.

One of ordinary skill in the art can select substrate thickness, porosity, and pore size
distribution using techniques known in the art. Desired substrate thickness, porosity and

pore size distribution can be selected based on, among other factors, the operating conditions of the final composite gas separation module such as operating pressure. Substrates having generally higher porosities and generally smaller pore sizes are particularly suited for producing composite gas separation modules. In some embodiments, the substrate can
5   have a porosity in a range of about 5 to about 75% or about 15 to about 50%. While the pore size distribution of a substrate can vary, the substrate can have pore diameters that range from about 0.1 microns or less to about 15 microns or more. Generally, smaller pore sizes are preferred. In some embodiments, the mean or median pore size of the substrate can be about 0.1 to about 15 microns, e.g., from about 0.1 to about 1, 3, 5, 7 or about 10
10   microns. For example, the substrate can be an about 0.1 micron grade substrate to an about 0.5 micron grade substrate, e.g., 0.1 micron, 0.2 micron, and 0.5 micron grades of stainless steel substrates can be used. In one embodiment, the substrate is 0.1 micron grade HASTELLOY® alloy.

        The composite gas separation module also includes an intermediate porous metal
15   layer, wherein the intermediate porous metal layer overlies the porous metal substrate. In one embodiment, for example, the intermediate porous metal layer has a top side and a bottom side and the intermediate porous metal layer is directly adjacent to the porous metal substrate on the bottom side and is directly adjacent to the dense hydrogen-selective membrane on the top side.

20   The intermediate porous metal layer can include palladium. For example, the intermediate porous metal layer can include palladium and a Group IB metal, e.g., palladium and copper or palladium and silver. In one embodiment, the intermediate porous metal layer includes alternating layers of palladium and the Group IB metal. For example, the composite gas separation module can include an intermediate porous metal layer having
25   alternating layers of palladium and silver in conjunction with a palladium or a palladium/silver alloy dense hydrogen-selective membrane, or the composite gas separation module can include an intermediate porous metal layer having alternating layers of palladium and copper in conjunction with a palladium or a palladium/copper alloy dense hydrogen-selective membrane.

30   In one embodiment, the intermediate porous metal layer may be formed by a method that includes electroless plating. For example, alternating layers of palladium and a Group IB metal can be applied using electroless plating.

In one embodiment, the intermediate porous metal layer contains about three to about six layers of palladium that alternate with about 2 to about 4 layers of the Group IB metal. The thickness of the individual alternating layers can be about 0.05 to about 5 microns thick, *e.g.*, about 0.1 to about 4 microns, about 0.2 to about 3 microns, or about 0.3 to about 1.5 microns. Examples of the order of the deposited layers include, but are not limited to, Pd-Ag-Pd-Ag-Pd and Pd-Ag-Pd-Ag-Pd-Pd-Ag-Pd-Ag-Pd.

In one embodiment, the intermediate porous metal layer is at least about 1, 2, 3, 4, or at least about 5 microns thick. For example, the intermediate porous metal layer can be about 1 to about 10, about 4 to about 8, or about 4 to about 6 microns thick. In one embodiment, the intermediate porous metal layer is not significantly less porous to helium gas flux than the porous substrate. In another embodiment, the intermediate porous metal layer is not significantly less porous to helium gas flux than the porous substrate. The intermediate porous metal layer can have a mean pore size that is less than the mean pore size of the porous metal substrate. In one embodiment, the largest pore of the intermediate porous metal layer is smaller than the largest pore of the porous metal substrate.

The intermediate porous metal layer can protect against intermetallic diffusion between the porous metal substrate and the dense gas-selective membrane. In some embodiments, intermetallic diffusion can occur between the porous metal substrate and the intermediate porous metal layer, but this diffusion does not substantially impair the performance of the dense gas-selective membrane. Without wishing to be held to any particular theory, intermetallic diffusion between the intermediate porous metal layer and the dense gas-selective membrane is not thought to be harmful to the gas selectivity of the membrane. In some embodiments, intermetallic diffusion between the intermediate porous metal layer and the dense gas-selective membrane enhances the permeability of the membrane. For example, the formation of a palladium alloy via diffusion of intermediate porous metal layer atoms into a dense hydrogen-selective membrane can enhance the hydrogen permeability of a dense hydrogen-selective membrane that includes palladium or alloy thereof. In one embodiment, the intermediate porous metal layer includes palladium and a Group IB metal, the dense gas-selective membrane includes palladium, and intermetallic diffusion of either or both of palladium and the Group IB metal from the intermediate porous metal layer into the dense gas-selective membrane improves the selective gas permeation through the membrane. Preferably, in one embodiment, the intermediate porous metal layer does not contain a concentration of a material which causes a substantial reduction in

the performance of the dense gas-selective membrane upon diffusion of that material into the membrane.

The intermediate porous metal layer used herein can improve adhesion of the dense gas-selective membrane to the porous metal substrate. For example, during a gas separa-
5   tion operation, the composite gas separation modules described herein can avoid membrane blistering, delamination and/or cracking even when operating at high temperatures and/or for extended periods of time. Without wishing to be held to any particular theory, the improvement in adhesion is thought to result from inter-diffusion of the metal particles of the intermediate porous metal layer and/or intermetallic diffusion between the intermediate
10 porous metal layer and the porous metal substrate on one side and the dense gas-selective membrane on the other side. For example, inter-diffusion can occur when the composite gas separation module is heated to operational temperatures (e.g., about 350°C to about 600°C).

The composite gas separation module can further include a substrate surface treat-
15 ment underlying the intermediate porous metal layer, as described infra. For example, a layer of a ceramic can be bonded to the porous metal substrate and underlie the intermediate porous metal layer. The ceramic can include oxides, nitrides, and/or carbides, for example, iron oxide, iron nitride, iron carbide and/or aluminum oxide.

The composite gas separation module can also further comprise a layer of a metal
20 selected from the group consisting of palladium, gold and platinum, wherein the layer of metal overlies the porous metal substrate and/or a substrate surface treatment and underlies the intermediate porous metal layer.

The composite gas separation module includes a dense gas-selective membrane, wherein the dense gas-selective membrane overlies the intermediate porous metal layer. In
25 one embodiment, the dense gas-selective membrane is selectively permeable to hydrogen, e.g., the dense gas-selective membrane is a dense hydrogen-selective membrane and can include one or more hydrogen-selective metals or alloys thereof. "Hydrogen-selective metals" include, but are not limited to, niobium (Nb), tantalum (Ta), vanadium (V), palladium (Pd), zirconium (Zr) and hydrogen-selective alloys thereof. Palladium and alloys of
30 palladium are preferred. For example, palladium can be alloyed with at least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium.

Where the gas separation module is to be used at temperatures below about 300°C, the dense gas-selective membrane can be formed of a palladium alloy such as, for example, an alloy of about 75 to about 77 weight percent palladium and about 25 to about 23 weight percent silver. An alloy is typically preferred at low temperatures because pure palladium

5   can undergo a phase change in the presence of hydrogen at or below about 300°C and this phase change can lead to embrittlement and cracking of the membrane after repeated cycling in the presence of hydrogen.

In one embodiment, the dense gas-separation membrane can include one or more non-metallic components. In another embodiment, the dense gas-separation membrane can

10   include one or more components that are not gas-selective materials, *e.g.*, components that are not hydrogen-selective materials.

In one embodiment, the thickness of the dense gas-selective membrane is less than about 3 times the diameter of the largest pore of the porous substrate. For example, the thickness of the dense gas-selective membrane can be less than about 2.5, 2, or less than

15   about 1.5 times the diameter of the largest pore of the porous substrate. While the thickness of the dense gas-selective membrane can depend, among other factors, on the size of the largest pores in the porous substrate, in some embodiments the dense gas-selective membrane is less than about 25, 20, 15, 12 or less than about 10 microns in thickness. For example, in one embodiment, the thickness of the dense gas-selective membrane is less

20   than about 14 microns such as about 3 to 14 microns. In one particular embodiment, the dense gas-selective membrane is of substantially uniform thickness.

In a particular fabrication method which can be used for making the present module, any contaminants are initially cleaned from the substrate, for example, by treating the substrate with an alkaline solution such as by soaking the substrate in an approximately

25   60°C ultrasonic bath for about half an hour. Cleaning is typically followed by rinsing such as, for example, wherein the substrate is sequentially rinsed in tap water, deionized water and isopropanol. Preparation of the porous substrate can also include surface treatment; formation of an additional intermetallic diffusion barrier such as by oxidizing the substrate, described *infra*; surface activation; and/or deposition of a metal such as palladium, gold or

30   platinum, as described *infra*, prior to applying the intermediate porous metal layer over the porous metal substrate.

The intermediate porous metal layer is applied over the porous metal substrate prior to application of a dense gas-selective membrane. In one embodiment, the intermediate

porous metal layer is formed by depositing palladium and Group IB metal over the porous metal substrate. For example, palladium and silver can be deposited as an intermediate porous metal layer and a palladium or palladium/silver alloy dense selective membrane can be subsequently applied, or palladium and copper can be deposited as an intermediate po-

5 rous metal layer and a palladium or a palladium/copper dense hydrogen-selective membrane can be subsequently applied. In one embodiment, the palladium and/or Group IB metal are deposited using electroless plating.

In one embodiment, the intermediate porous metal layer is applied by depositing alternating layers of palladium and a Group IB metal over the porous metal substrate. For

10 example, palladium can be applied to a porous metal substrate, followed with an application of silver or copper, followed with an application of palladium, followed with an application of silver or copper, and so on. In one embodiment, palladium and a Group IB metal are electrolessly plated onto a support without rinsing, activation, drying and/or sintering of the support between sequential applications of the metals. Without wishing to be held to

15 any particular theory, it is believed that sequential electroless deposition of layers of palladium and/or a Group IB metal without intermediate rinsing, activation, drying and/or sintering can produce particles, e.g., nano-size particles, of palladium and/or the Group IB metal.

In one embodiment, the surface of the intermediate porous metal layer is abraded,

20 e.g., treated mechanically, thereby forming a polished substrate, prior to application of the dense gas-selective membrane over the intermediate porous metal layer. Mechanical treatment of the intermediate porous metal layer can include, for example, brushing the surface of the intermediate porous metal layer with a plastic bristle brush having a toothbrush-like consistency or gently polishing the surface with a fine emery cloth. By

25 mechanically treating the intermediate porous metal layer, the roughness of the surface can be improved by, for example, removing relatively large particles (e.g., a Pd/Group IB metal agglomeration) from the surface of intermediate porous metal layer. In one embodiment, about 5 to about 10 weight percent of the deposited intermediate porous metal layer is removed by abrasion. Abrasion of a deposited material is further described infra.

30 In one embodiment, the method for fabricating the module can include the step of depositing a hydrogen-selective metal on the intermediate porous metal layer, thereby forming a coated substrate and abrading the surface of the coated substrate, thereby form-

ing a polished substrate, prior to formation of the dense gas-selective membrane (*e.g.*, a dense hydrogen-selective membrane) over the intermediate porous metal layer.

Following application of the intermediate porous metal layer, a dense gas-selective membrane is applied over the intermediate porous metal layer. For example, a dense gas-
5   selective membrane can be applied by depositing a gas-selective metal, *e.g.*, a hydrogen-selective metal, over the intermediate porous metal layer. In one embodiment, palladium or an alloy thereof is deposited, *e.g.*, electrolessly plated, over the intermediate porous metal layer, thereby forming a dense gas-selective membrane. Application of the dense gas-selective membrane can include surface activating the intermediate porous metal layer
10   prior to depositing dense gas-selective membrane components.

Components of the dense gas-selective membrane, *e.g.*, a hydrogen-selective metal or an alloy thereof, can be deposited over the intermediate porous metal layer using any of the techniques known in the art for depositing such materials on a support. For example, a component of the dense gas-selective membrane can be deposited on the support using
15   electroless plating, thermal deposition, chemical vapor deposition, electroplating, spray deposition, sputter coating, e-beam evaporation, ion beam evaporation or spray pyrolysis.

An alloy of a gas-selective metal can be deposited over the intermediate porous metal layer as a component of the dense gas-selective membrane. In one embodiment, a palladium/silver alloy is formed by first depositing palladium onto the support by elec-
20   troless deposition and then depositing silver, also by electroless deposition, onto the support. An alloy membrane layer can then be formed by heating the silver and palladium layers, for example, to about 500°C to about 1000°C in an inert or hydrogen atmosphere. In one embodiment, metal components can be co-deposited onto the support to form a layer of a finely divided mixture of small pockets of the pure metal components. In an-
25   other embodiment, a technique such as sputtering or chemical vapor deposition is used to simultaneously deposit two or more metals to form an alloy layer on the support.

In one embodiment, a small quantity of the metal, sufficient to cover the pore walls of the substrate, for example less than about 10, 7, 5, 3 or 1 percent of the ultimate thickness of the dense gaseous membrane, is deposited on the porous substrate without a sig-
30   nificant reduction of the substrate porosity. Typically, the deposition of palladium, gold and/or platinum on the porous substrate is made by surface activating and plating on the side of the substrate opposite to the side on which a gas-selective membrane will be formed. For example, in one embodiment, a deposit of palladium, gold and/or platinum is

formed from the inside of a substrate tube (*e.g.*, using an electroless plating solution) and a dense gas-selective membrane is subsequently formed on the outside of the substrate tube. The gas separation modules can also be fabricated by selectively surface activating a support proximate to a defect and preferentially depositing a material on the selectively surface activated portion of the support. The method is discussed in "Method for Curing Defects in the Fabrication of a Composite Gas Separation Module," U.S. Application Serial No. 10/804,848 filed March 19, 2004.

In one embodiment, the invention includes removing residual metal chlorides, for example, by treatment with an aqueous phosphoric acid solution, *e.g.*, 10% phosphoric acid solution. For example, the treatment can include application of 10% phosphoric acid solution at room temperature for a time sufficient to convert residual metal chlorides to metal phosphates, *e.g.*, about 30 minutes, followed by appropriate rinsing and drying, *e.g.*, rinsing with deionized water for about 30 minutes and drying at about 120°C for at least about 2 hours.

In some embodiments, the composite gas separation modules are made by one or more of the following steps:(i) substrate surface treatments by oxidizing the surface of the substrate or by forming a nitride layer, (ii) surface activation of the support, e.g. with aqueous stannous chloride and palladium chloride prior to deposition of metal membrane, or (iii) metal deposition over the support or the intermediate layer, which steps are described in U.S. Patent No. 6,152,987, and also in U.S. Patent Application No.10/804,848; U.S. Patent Application No. 10/804,847, entitled "Method for Fabricating Composite Gas Separation Modules," filed on March 19, 2004; U.S. Patent Application No. 10/836,088, entitled "High Tamman Temperature Intermediate Layer", filed on April 30, 2004; U.S. Patent Application No. 10/896,743, filed July 21, 2004.

The following illustrative embodiments will serve to illustrate the invention disclosed herein. The examples are intended only as a means of illustration and should not be construed as limiting the scope of the invention in any way. Those skilled in the art will recognize many variations that may be made without departing from the spirit of the disclosed invention.

ILLUSTRATIVE EMBODIMENT 1

Figure 4 shows a schematic diagram of a multi-tubular, DC heated, radial flow, membrane, steam reforming reactor in accordance with the present invention. In the reactor shown in Figure 4, a vaporizable hydrocarbon and steam enter the reactor at inlet 69 and

flow through the reforming catalyst bed 70 (which is in the form of an annulus) containing multiple membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) and multiple DC tubes 72 surrounded by the catalyst bed. In this embodiment the feed gases and reaction gases flow through the catalyst bed
5 radially from outside to inside. The multiple hydrogen-selective, hydrogen-permeable, membrane tubes 71 are disposed axially in concentric rows in the reforming catalyst bed and serve to remove hydrogen, which is produced by the reforming reactions. The multiple DC tubes (i.e., chambers) 72 are also disposed axially in concentric rows in the reforming catalyst bed (for example, in a ratio of 1:2 or other number of DC tubes to the number of
10 membrane tubes). The multiple DC tubes are in contact with the reforming catalyst bed and provide a controlled, distributed heat flux to the catalyst bed sufficient to drive the reforming reactions. While the membrane tubes and the DC tubes are shown to be in concentric rows in Figure 4, other geometric arrangements of these tubes can be suitably employed, and are within the scope of the present invention.

15   The DC tubes 72 generally comprise a fuel conduit disposed within a larger tube with an inlet and flow path for a preheated oxidant (e.g., preheated air) and an outlet for combustion (flue) gas. The DC tubes may be closed ended with a fuel conduit, oxidant inlet and flow path, and flue gas outlet arranged as shown in Figure 6A, or may open ended with the fuel conduit, oxidant inlet and flow path arranged as shown in Figure 6B.

20   High purity hydrogen is removed from the multi-tubular, radial flow, reactor shown in Figure 8 via outlets 73, with the aid of vacuum. Optionally, a sweep gas may be used to promote the diffusion of hydrogen through the membrane of the membrane tubes 71. If a sweep gas is employed, the membrane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as discussed in Figure 12. By-product
25 gases, including unpermeated hydrogen, if not further used internally for heat production, e.g., combustion or heat exchange, exit the multi-tubular, radial flow, reactor via outlet 74. A hollow tube or cylinder 75 may optionally be used for flow distribution.

ILLUSTRATIVE EMBODIMENT 2

        Figure 5 is a top cross-section view of the shell of the multi-tubular, DC heated,
30 radial flow, membrane, steam reforming reactor of Figure 4. The cross sectional view of the reactor shows multiple membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Ilustrative Embodiment 12) and multiple DC tubes 72 dispersed in catalyst bed 70 with optional hollow tube or cylinder 75 being in the center of the reactor.

In the example shown, the membrane tubes 71 have outside diameters (OD) of about one

inch (2.5 cm) while DC tubes have an OD of approximately two inches (5.1 cm), although

other sizes of these tubes can be suitably employed. If a sweep gas is employed, the mem-

brane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for

5   sweep gas and hydrogen as shown in Figures 8 and 13. A larger shell containing more

tubes duplicating this pattern can also be used.

ILLUSTRATIVE EMBODIMENT 3

Figures 6A and 6B are schematic diagrams showing an example of a "closed

ended" and of an "open ended" distributed combustion tubular chamber which are used to

10   drive the reforming reactions in various embodiments of the present invention. Referring to

Fig. 6A, an oxidant (in this case preheated air) enters the DC tube at inlet 76 and mixes

with fuel which enters the DC tube at inlet 77 and passes into fuel conduit 78 through noz-

zles 79 spaced along the length of the fuel conduit, whereupon it mixes with the air which

has been preheated to a temperature such that the temperature of the resulting mixture of

15   fuel and air is above the autoignition temperature of the mixture. The reaction of the fuel

passing through the nozzles and mixing with the flowing preheated air at a temperature

above the autoignition temperature of the mixture, results in distributed combustion which

releases controlled heat along the length of the DC tube as shown, with no flames or hot

spots. The combustion gases, (i.e., flue gas) exit the DC tube at outlet 80.

20   In the "open ended" DC tubular chamber shown in Fig. 6B, preheated air enters the

DC tube at inlet 76 and the fuel at inlet 77, and the fuel passes through conduit 78 and noz-

zles 79, similar to "closed end" DC tube in Fig. 6A. However, in the case of the "open

ended" DC tube, the flue gas exits the DC tube at open end 81, instead of outlet 80 as

shown in Fig.6A.

25   ILLUSTRATIVE EMBODIMENT 4

Figure 7 is a schematic drawing of a multi-tubular, DC heated, axial flow, mem-

brane, steam reforming reactor in accordance with the present invention. In the reactor

shown in Figure 7, a vaporizable hydrocarbon and steam enter the reactor at inlet 69 and

flow through the reforming catalyst bed 70 containing multiple hydrogen- selective mem-

30   brane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustra-

tive Embodiment 12) and multiple DC tubes 72. In this embodiment the feed gases and re-

action gases flow through the catalyst bed axially from the top of the catalyst bed to the

bottom. The multiple hydrogen-selective membrane tubes 71 are disposed axially in the

reforming catalyst bed and serve to remove hydrogen which is produced by the reforming reactions. In the embodiment shown the membrane tubes are closed at the top and a sweep gas (e.g. steam) is employed, which enters the reactor at inlet 85 into the bottom of the membrane tubes where it flows upward in the outer part of the membrane tube, counter-

5 current to the hydrocarbon and steam feed. A stinger pipe fitted to the bottom of the per-meate section may be used to distribute the sweep gas in the membrane tube. The perme-ated hydrogen and sweep gas flow downward in a return tube located in the center of the membrane tube and exit the reactor via outlet 86. The pressure drop in the permeate pipe section is significant when the length of the pipe relative to the diameter exceeds a given

10 limit. Actually, the volumetric amount of hydrogen crossing the membrane is proportional to the membrane area, $\Box *D*L$ and the multiplier is the velocity, which is fixed as a func-tion relating to Sievert's law, the description of which can be found in US2003/0068269. The same hydrogen amount has to flow across the pipe cross section which is equal to $\pi *D^2/4$. The ratio of hydrogen velocities through the pipe and through the membrane re-

15 spectively is proportional to $(\pi *D*L)/(\pi *D^2/4)$ or to L/D. Pressure drop increases with gas velocity. If this ratio exceeds a limit, then the velocity in the permeate pipe exceeds a limit too, since the velocity through the membrane is fixed. Then the pressure drop in the permeate pipe becomes high and it reduces the hydrogen flux by creating back pressure in the permeate section. In such a case, the reactor design has to accommodate either a higher

20 membrane diameter, or a reduced length.

There are also multiple DC tubes (i.e., chambers) 72 disposed axially in the reform-ing catalyst bed. In the embodiment shown the DC tubes are "closed ended" tubes with preheated air entering at inlet 76, fuel entering at 77 and combustion gas (i.e., flue gas) ex-iting the reactor at outlet 80. The multiple DC tubes are in heat transferring contact with

25 the reforming catalyst bed 70 and provide a controlled, distributed heat flux to the catalyst bed sufficient to drive the reforming reactions. While the membrane tubes and the DC tubes are shown to be in a particular geometric pattern in Figure 11, it is understood that other geometric arrangements of these tubes may be used and are within the scope of the invention. While "closed ended" DC tubes are employed in the particular reactor shown in

30 Figure 7, "open ended" DC tubes may be suitably employed as well. Also, the DC tubes and/or the membrane tubes may be surrounded by cylindrical screens (not shown) to pro-tect them from getting in direct contact with the catalyst, and allow insertion of these tubes even after the catalyst is loaded into the reactor.

The DC chamber must be free of obstructions and have a tubular dimension for the external or exterior tube of the DC chamber such that the length to diameter ratio is higher than a given limit, preferably more than 4. This ratio ensures that the air velocity in the chamber becomes higher than the flame velocity of the fuel and that turbulence is induced

5   to improve heat transfer. In such a condition, no flames are created or stabilized. Any obstructions (like baffles) would create stagnation points where flames would form and stabilize.

High purity hydrogen, which diffuses through the membrane into the membrane tubes, is removed from the reactor via outlet(s) 86 together with the sweep gas (in this case

10   steam). While outlet 86 is shown in Figure 7 to be located on the side of the reactor, this outlet may optionally be located at the bottom of the reactor thereby avoiding a bottom side exit manifold. A further option involves the use of a vacuum instead of a sweep gas to facilitate diffusion of the hydrogen through the membrane into the membrane tubes. Vacuum can be induced either mechanically with a pump or chemically with a metal hydride

15   precursor which reacts away the hydrogen to form metal hydride. The hydride is on-line for a given period of time and when it is saturated, a parallel compartment can be put on-line, while the original compartment is isolated and heated to desorb and produce the hydrogen. This is advantageous in cases where the hydrogen needs to be stored and/or shipped to a customer or in cases where the cost of electrical energy for running a pump is

20   higher than using waste energy to desorb the hydrogen from the hydride. Detailed economics will dictate the right choice.

In another embodiment of the reactor in Figure 7, the sweep gas inlet 85 and the hydrogen, sweep gas outlet 86 and their associated plenums, may be placed on the top of the reactor allowing easy access to the bottom of the reactor. In a further embodiment of

25   the reactor of Figure 11, the preheated air inlet 76, the fuel inlet 77 and the flue gas outlet 80 and their associated plenums may be placed on the bottom of the reactor allowing easy access to the top of the reactor.

By-product gases, including carbon dioxide, steam, and minor amounts of carbon monoxide and unpermeated hydrogen, if not further used internally for heat production,

30   e.g., combustion or heat exchange, exit the multi-tubular, axial flow, reactor via outlet 74. The reactor shown in Fig. 11 may be equipped with baffles and/or screens such as the baffles shown in Figures 13A and 13B or 13C and 13D.

ILLUSTRATIVE EMBODIMENT 5

Figure 8 is a top cross-section view of the shell of the multi-tubular, DC heated, axial flow, membrane reactor shown in Figure 7. In the embodiment shown multiple membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustra-

5 tive Embodiment 12) and multiple DC tubes 72 are dispersed in reforming catalyst bed 70. The multiple DC tubes employed in this embodiment are "closed ended" DC tubes as discussed above in connection with Figure 7. The membrane tubes are equipped with an outer sweep gas feed tube and an inner hydrogen, sweep gas return tube as discussed in connection with Figure 7. A typical reactor of the type shown in this Figure 8 may comprise, for

10 example, 19 DC tubes of 5.5" (14 cm) outer diameter and 90 membrane tubes of 2" (5.1 cm) outer diameter enclosed in a shell of 3.5 ft (1.1 m) diameter containing catalyst in the void spaces. Other shell sizes and numbers of tubes can be suitably employed depending on the capacity needed. The design parameter which is of utmost importance is the optimum gap between the membrane and the DC tubes. If a high gap is assumed, then heat

15 transfer limitations occur since the flow of enthalpy from DC to the reforming reaction is slow. The membranes may not operate isothermally and cold spots may develop, thus reducing the reactor efficiency. If a small gap is assumed, then there may be problems with insufficient catalyst penetration in the gap, overheating of the membrane, or even touching of the hot DC tube with the membrane in conditions where the tubes are not perfectly

20 straight. A narrow gap limitation will make reactor fabrication more expensive, since clearances are hard to achieve. Thus, an intermediate gap is more preferable. As a particular non-limiting example, the gap between the membrane and the DC tubes is from about ¼ inch (about 0.64 cm) to about 2 inches (about 5.08 cm), particularly from about ½ inch (about 1.27 cm) to about 1 inch (about 2.54 cm). The gap between the membrane tubes

25 may be from about ¼ inch to about 2 inches, particularly from about ½ inch to about 1 inch and this has to be also optimized. The hydrogen-permeable membrane tube has a ratio of length to diameter of less than about 500.

ILLUSTRATIVE EMBODIMENT 6

Figures 9A and 9B and 9C and 9D show two different configurations of baffles

30 which may be employed in the multi-tubular, DC heated, axial flow, membrane steam reforming reactors of the invention to increase contact of the reactant gases with the catalyst in the catalyst beds. The baffle configuration shown in Figures 9A and 9B comprise a washer shaped baffle 87 and a disk shaped baffle 88 arranged in an alternating pattern. This

baffle arrangement causes the feed and reactant gases to flow through the hole in the washer shaped baffle and be deflected by disk shaped baffle thereby enhancing the contact of the reactant gases with the catalyst (not shown) which is packed in the area between the baffles.

5   The baffle arrangement shown in Figures 9C and 9D comprises truncated disks 89 which are placed in an alternating pattern (truncated left and truncated right) in the reactor thereby causing the feed and reactant gases to "zigzag" as they flow through the catalyst (not shown) which is packed in the area between the baffles.

    The baffles in Figures 9A&B and 9C&D will have openings (not shown) to allow

10 the DC tubes and membrane tubes to pass through them. Screens positioned in vertical alignment (not shown) may also be used to support the baffles and in some cases hold the catalyst away from the shell wall or from the center of the shell for better gas flow distribution.

ILLUSTRATIVE EMBODIMENT 7

15   Figure 13 is a top cross-section view of the shell of a multi-tubular reactor in accordance with one embodiment of the invention in which four membrane tubes 71(made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) are dispersed in the reforming catalyst bed 70 which is packed into reactor tube 82, while the DC chamber is in the form of an annulus surrounding the reforming catalyst bed. The tubular

20 DC chamber (which is defined by outer wall 83 and the wall of the reactor tube 82) contains multiple fuel conduits 78 having nozzles (not shown) through which fuel flows and mixes with preheated air flowing in the DC chamber whereupon combustion occurs. If a sweep gas is employed, the membrane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as shown in Figure 13. In one em-

25 bodiment of the invention, the membrane tubes have an outer diameter of 2 inches (5.1 cm), while the outer DC tube has an inner diameter of approximately 8.6 inches (21.8 cm). However, other sizes can be suitably employed.

ILLUSTRATIVE EMBODIMENT 8

    Figure 10 is a top cross-section view of the shell of another embodiment of the

30 multi-tubular, axial flow, reactor of the invention in which multiple reactor tubes 82 packed with reforming catalyst are employed. In this example each of the six reactor tubes 82 contains a catalyst bed 70 and a membrane tube 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) containing an outer sweep gas

feed tube and an inner hydrogen, sweep gas return tube. Heat is provided to the reforming catalyst beds by the tubular DC chamber defined by outer wall 83 and inner wall 84. The DC chamber contains multiple fuel conduits 78 dispersed at various intervals in the DC chamber. A hollow tube or cylinder defined by inner wall 84 may optionally be used for

5   flow distribution.

ILLUSTRATIVE EMBODIMENT 9

Figure 12 is a top cross-section view of the shell of a further embodiment of the multi-tubular, axial flow, reactor of the invention in which four membrane tubes are dispersed in each of six reactor tubes 82 containing catalyst beds 70. Heat is provided to the

10   catalyst beds by DC chamber defined by outer wall 83 and inner wall 84. The DC chamber contains multiple fuel conduits 78 having nozzles 79 (not shown). If a sweep gas is employed, the membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12)may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as discussed above in connection with Figures 8

15   and 13. The hollow cylinder or tube defined by inner wall 84 may optionally be used for flow distribution.

ILLUSTRATIVE EMBODIMENT 10

Figure 12 is a top cross-section view of the shell of a further embodiment of the multi-tubular, axial flow, reactor of the invention in which six membrane tubes 71 (made

20   by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) are dispersed in each of the six reactor tubes 82 packed with reforming catalyst. Heat is provided to the reforming catalyst beds by the DC chamber defined by outer wall 83 and inner wall 84. The DC chamber contains multiple fuel conduits 78. Additional heat may be provided to the catalyst beds by employing an DC tube 72 in the center of each of the reactor

25   tubes 82 as shown in Figure 12. The hollow tube or cylinder defined by inner wall 84 may optionally be used for flow distribution.

If a sweep gas is employed, the membrane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as discussed in Figure 12.

ILLUSTRATIVE EMBODIMENT 11

30   This embodiment describes the fabrication of a composite structure which can be used for making the hydrogen-selective and hydrogen-permeable membrane tubes for the reactors of the Illustrative embodiments 1-10. It comprises palladium, an intermediate po-

rous metal layer (*e.g.*, a porous metal layer intermetallic diffusion barrier), and a 0.1 micron grade porous 316L stainless steel ("PSS") support.

A 6 inch (15.2 cm) long, 1 inch (2.5 cm) outer diameter, section of PSS tube, welded to sections of 1 inch (2.5 cm) outer diameter dense, non-porous 316L stainless steel

5   tube on each end, was obtained from Mott Metallurgical Corporation. Contaminants were removed by cleaning the tube in an ultrasonic bath with alkaline solution at 60°C for one half hour. The tube was then sequentially rinsed using tap water, deionized water and isopropanol.

The tube was oxidized in static air at 400°C for 12 hours wherein the rates of heat-

10   ing and cooling were 3°C per minute. The oxidized tube was then surface activated by sequentially immersing the tube in aqueous baths of $SnCl_2$ and $PdCl_2$. The tube was immersed in 500 mL of aqueous $SnCl_2$ (1 g/L) at 20°C for about 5 minutes and was subsequently rinsed with deionized water. The tube was then immersed in 500 mL of aqueous $PdCl_2$ (0.1 g/L) at 20°C for about 5 minutes followed by rinsing first with 0.01 molar hy-

15   drochloric acid and then with deionized water. The above-described surface activation cycle was performed a total of five times followed by drying for 2 hours at 120°C.

An intermediate porous metal layer of palladium and silver was then applied to the surface activated tube. Thin layers of palladium (Pd) and silver (Ag) were sequentially deposited using electroless plating as described below.

20   Palladium layers were deposited on the tube by electroless plating according to the following procedure. The tube was immersed in a plating solution at room temperature. The plating solution was composed of 4 grams $Pd(NH_3)_4Cl_2 \cdot H_2O$/liter, 198 milliliters NH_4OH (28 weight percent)/liter, 40.1 grams Na_2EDTA/liter, and 6 milliliters H_2NNH_2 (1 M)/liter. The plating solution and tube were placed in a water bath at 60°C. After the plat-

25   ing solution was depleted, the tube was removed and rinsed with deionized water at 60°C with 4 to 5 rinses.

Silver layers were deposited on the tube by electroless plating according to the following procedure. The tube was immersed in a plating solution at room temperature. The plating solution was composed of 0.519 grams $AgNO_3$/liter, 198 milliliters NH_4OH (28

30   weight percent)/liter, 40.1 grams Na_2EDTA/liter, and 6 milliliters H_2NNH_2 1 M)/liter. The plating solution and tube were placed in a water bath at 60°C. After the plating solution was depleted, the tube was removed and rinsed with deionized water at 60°C with 4 to 5 rinses.

Each metallic layer was applied by contacting the tube with a plating solution for 90 minutes and was followed by rinsing the tube with deionized water, but not with intermediate activation, drying or sintering. The specific layers, an estimate of the layer thicknesses, and the order of their application were Pd (about 1.5 microns), Ag (about 0.3 mi-

5   crons), Pd (about 1 micron), Ag (about 0.3 microns), and Pd (about 1.5 microns) (a total of five layers). (Thickness estimates were based on time of contact with the plating solutions. The average rate of metal deposition was determined for a test piece of a similar support and the identical plating solution and activation procedure. The test pieces were activated, then plated for 90 minutes and then rinsed, dried and weighed. From that it was possible to

10   estimate the thickness which was deposited over 90 minutes.) After applying the above-described palladium and silver layers, the membrane was dried at 120°C for about 48 hours. Helium flux was measured across the membrane thus formed. These measurements indicated that the membrane was not gas tight at this point.

The membrane surface was then lightly brushed with a fine artist's paint brush.

15   Following this brushing, the entire plated surface of the tube was dipped in 0.1M HCL for 60 seconds at room temperature. The membrane was then rinsed with deionized water at room temperature. Then, the membrane was surface activated by repeating the surface activation cycle, described *supra*, three times. The membrane was then dried at 120°C overnight.

20   Palladium was then deposited on the exterior of the tube by electroless plating according to the above-described procedure three times for 90 minutes each time (a total of 4.5 hours). Between each of the 90 minute platings, the membrane was rinsed with deionized water (at 60°C) not less than three times. After the last plating and rinsing with DI water, the membrane was dried for 2 hours at 120°C.

25   Defects (*e.g.*, pores) present in the tube were then selectively surface activated from the inside of the tube. Aqueous solutions of $SnCl_2$ (1 g/L) and $PdCl_2$ (0.1 g/L) were sequentially supplied to the inside surface of the tube. The inside of the tube was filled with the $SnCl_2$ solution at 20°C for about 5 minutes followed by subsequent rinsing with deionized water. The tube was then filled with the $PdCl_2$ solution at 20°C for about 5 minutes

30   followed by rinsing first with 0.01 molar hydrochloric acid and then with deionized water. This selective surface activation cycle was performed a total of five times followed by drying for 2 hours at 120°C.

The tube was then plated with three layers of palladium from the outside of the tube using the palladium plating procedure described *supra*. Following this further palladium plating, the inside of the tube was treated with a 10% phosphoric acid solution for about 30 minutes and then rinsed with deionized water and thoroughly dried at 120°C. The proc-

5 esses of selectively surface activating the tube from the inside, plating with palladium from the outside of the tube, and treating with phosphoric acid solution were repeated once.

The membrane was then lightly dry sanded with 2400 grit waterproof sand paper (SILICON CARBIDE, Struers, Inc., Westlake, OH). Following this, it was rinsed in acetone with a mild ultrasonic treatment for 15 minutes and then dried overnight at 120°C.

10 The membrane was then surface activated, as described above, by repeating the general surface activation cycle on the exterior of the tube three times. Palladium was then deposited on the exterior of the tube by electroless plating according to the above-described procedure four times for 90 minutes each time (a total of six hours). Between each of the 90 minute platings, the membrane was rinsed with deionized water (at 60°C)

15 not less than three times and the plating solution was replaced with a fresh plating solution. Following the final palladium plating, the membrane was rinsed with deionized water and thoroughly dried at 120°C.

Based on gravimetric data, the total palladium and silver thickness of the finished membrane was 24 microns.

20 The membrane was tested for hydrogen permeation at 500°C with a 1 atmosphere pressure differential for a cumulative total of 608 hours. During the first 501 hours of continuous testing, the hydrogen permeance measured under these conditions rose from 15.7 to 17.6 normal cubic meters per square meter per hour (reference temperature = 0°C, reference pressure = 1 atmosphere) $(Nm^3/m^2\text{-hr})$ at 24 hours and 501 hours, respectively. The sepa-

25 ration factor at the end of the first 501 hour continuous test was estimated to be about 180 based on a helium leak measurement taken at 500°C at 501 hours. During a second round of testing, no decline in the hydrogen permeance was observed for an additional 107 hours of testing. The membrane was observed to obey Sievert's law at 373, 449, and 498°C for flux measurements taken with a pressure difference between 0.25 and 2.7 atmospheres.

30 Thus, under these conditions, hydrogen permeation was limited by the diffusion of hydrogen atoms through the palladium. The activation energy obtained from hydrogen permeance measurements taken with a 1 atmosphere pressure difference over the temperature range of 366°C to 500°C was 10.9 kJ/mol.

ILLUSTRATIVE EMBODIMENT 12

This embodiment describes the fabrication of a composite structure which can be used for making the hydrogen-selective and hydrogen-permeable membrane tubes for the reactors of the Illustrative embodiments 1-10. It comprises palladium, an intermediate po-
5   rous metal layer (e.g., a porous metal layer intermetallic diffusion barrier), and a 0.1 mi-cron grade porous 316L stainless steel ("PSS") support. A hydrogen selective membrane was formed on a 40 inch (101 cm) long section of 1 inch (2.5 cm) outer diameter PSS us-ing procedures substantially the same as those described in Illustrative Embodiment 11.

The total palladium and silver thickness of the finished membrane (the total noble
10   metal thickness) was 25.5 microns, determined gravimetrically. The membrane was tested for hydrogen permeation at 450°C and 500°C with a 1 atmosphere pressure differential. This membrane had hydrogen permeance of 5.05 Nm^3/m^2-hr at 450°C and 5.67 Nm^3/m^2-hr at 500°C. Based on these two permeance measurements, the activation energy was esti-mated to be about 10.8 kJ/mol.

15   ILLUSTRATIVE EMBODIMENT 13

This experiment illustrates the stability of an intermediate porous metal layer.

An intermediate porous metal layer of palladium and silver was deposited on a po-rous 316L stainless steel ("PSS") support. The support was a 6 inch (15.2 cm) long, 1 inch (2.5 cm) outer diameter section of 0.1 micron grade PSS tube, welded to sections of 1 inch
20   (2.5 cm) outer diameter dense 316L stainless steel tube on each end, obtained from Mott Metallurgical Corporation.
Contaminants were removed by cleaning the tube in an ultrasonic bath with alkaline solu-tion at 60°C for one half hour. The tube was then sequentially rinsed using tap water, de-ionized water and isopropanol.
25   The tube was oxidized in air at 400°C for 10 hours wherein the rates of heating and cooling were 3°C per minute. The oxidized tube was then surface activated by sequentially immersing the tube in aqueous baths of $SnCl_2$ and $PdCl_2$. The tube was immersed in 500 mL of aqueous $SnCl_2$ (1 g/L) at 20°C for about 5 minutes and was subsequently rinsed with deionized water. The tube was then immersed in 500 mL of aqueous $PdCl_2$ (0.1 g/L)
30   at 20°C for about 5 minutes followed by rinsing first with 0.01 molar hydrochloric acid and then with deionized water. The above described surface activation cycle was performed a total of five times followed by drying for 2 hours at 120°C.

An intermediate porous metal layer of palladium and silver was then applied to the surface activated tube. Thin layers of palladium (Pd) and silver (Ag) were sequentially deposited using electroless plating as described below.

Palladium layers were deposited on the tube by electroless plating according to the

5   following procedure. The tube was immersed in a plating solution at room temperature. The plating solution was composed of 4 grams $Pd(NH_3)_4Cl_2 \cdot H_2O$/liter, 198 milliliters NH_4OH (28 weight percent)/liter, 40.1 grams Na_2EDTA/liter, and 6 milliliters H_2NNH_2 (1 M)/liter. The plating solution and tube were placed in a water bath at 60°C. After the plating solution was depleted, the tube was removed and rinsed with deionized water at 60°C

10   with 4 to 5 rinses.

Silver layers were deposited on the tube by electroless plating according to the following procedure. The tube was immersed in a plating solution at room temperature. The plating solution was composed of 0.519 grams $AgNO_3$/liter, 198 milliliters NH_4OH (28 weight percent)/liter, 40.1 grams Na_2EDTA/liter, and 6 milliliters H_2NNH_2 (1 M)/liter.

15   The plating solution and tube were placed in a water bath at 60°C. After the plating solution was depleted, the tube was removed and rinsed with deionized water at 60°C with 4 to 5 rinses.

The intermediate porous metal layer of palladium and silver was formed with 17 layers of silver and 20 layers of palladium in three plating cycles. Each layer of palladium

20   or silver was applied by contacting the tube with a plating solution for 90 minutes and was followed by rinsing the tube with deionized water, but not with intermediate activation, drying or sintering within one cycle. Between cycles, the membrane was dried and the surface activation cycle was performed three times.

Five layers of silver and six layers of palladium were deposited in the first plating

25   cycle. The layer order of first plating cycle was Pd-Ag-Pd-Ag-Pd-Ag-Pd-Ag-Pd-Ag-Pd. In each of the second and third plating cycles six layers of silver and seven layers of palladium were deposited. The second and third plating cycles each had the following layer order: Pd-Ag-Pd-Ag-Pd-Ag-Pd-Ag-Pd-Ag-Pd-Ag-Pd.

The approximate layer thickness for each Pd layer was about 0.32 microns and for

30   each Ag layer was about 0.26 microns. (Thickness estimates were based on time of contact with the plating solutions. The average rate of metal deposition was determined for a test piece of a similar support and the identical plating solution and activation procedure. The

test pieces were activated, then plated for 90 minutes and then rinsed, dried and weighed. From that it was possible to estimate the thickness which was deposited over 90 minutes.)

Determined gravimetrically and not accounting for porosity, the total thickness of the palladium and silver layers was about 10.8 microns. Following deposition of the palla-
5   dium and silver layers, the membrane was porous as determined by helium flux measurements.

The tube was then plated with an additional 21.1 microns of palladium in two cycles over the intermediate porous metal layer of palladium and silver. The tube was plated using the palladium plating procedures described above.

10   The membrane was then surface activated, as described above, by repeating the surface activation cycle on the exterior of the tube three times. Palladium was then deposited on the exterior of the tube by electroless plating according to the above-described procedure five times for 90 minutes each time (a total of about 7.5 hours). Between each of the 90 minute palladium platings, the membrane was rinsed with deionized water (at 60°C) not
15   less than three times and the plating solution was replaced with a fresh plating solution. The membrane was thoroughly dried following application of the five plating solutions. Then, this procedure of surface activation, 7.5 hours of palladium plating, rinsing and drying was repeated once.

The resulting tube was then heated to 500°C and held at that temperature for 100
20   hours under flowing helium. At the end of this heat treatment, the membrane remained porous to helium which indicated that the intermediate porous metal layers formed by the methods of the present invention are stable at operational temperatures for hydrogen separation or membrane reactor applications.

ILLUSTRATIVE EMBODIMENT 14

25   This embodiment describes the fabrication of a composite structure which can be used for making the hydrogen-selective and hydrogen-permeable membrane tubes for the reactors of the Illustrative embodiments 1-10. It includes palladium, an intermediate porous metal layer, and a 0.1 micron grade porous HASTELLOY® C-22® support. (HASTELLOY® C-22® is a nickel-chromium-molybdenum-iron-tungsten alloy.)

30   A 31.3 inch (79.5 cm) long, 1 inch (2.5 cm) outer diameter, section of porous HASTEL-LOY® C-22® tube, welded to sections of 1 inch (2.5 cm) outer diameter dense, non-porous 316L stainless steel tube on each end, was obtained from Mott Metallurgical Corporation. Contaminants were removed by cleaning the tube in an ultrasonic bath with alkaline solu-

tion at 60°C for one half hour. The tube was then sequentially rinsed using tap water, deionized water and isopropanol.

The tube was oxidized in static air at 600°C for 12 hours. The rate of heating and cooling was 3°C per minute. Following oxidation, helium flux through the support was

5   measured to be 16.0 Nm^3/m^2-hr at a pressure difference of 1 atm (0.101 MPa) and a temperature of 20°C. Subsequent helium flux measurements were made under the same conditions.

The oxidized tube was then surface activated by sequentially immersing the tube in baths of $SnCl_2$ and $PdCl_2$. The tube was immersed in 3.5 L of aqueous $SnCl_2$ (1 g/L) at

10   20°C for about 5 minutes and was subsequently rinsed with deionized water. The tube was then immersed in 3.5 L of aqueous $PdCl_2$ (0.1 g/L) at 20°C for about 5 minutes followed by rinsing first with 0.01 molar hydrochloric acid and then with deionized water. The above-described surface activation cycle was performed a total of six times followed by drying overnight at 120°C.

15   An intermediate porous metal layer of palladium and silver was then applied to the surface activated tube. Thin layers of palladium (Pd) and silver (Ag) were sequentially deposited using electroless plating as described below.

Palladium layers were deposited on the tube by electroless plating according to the following procedure. The tube was immersed in a plating solution at room temperature.

20   The plating solution was composed of 4 grams $Pd(NH_3)_4Cl_2 \cdot H_2O$/liter, 198 milliliters NH_4OH (28 weight percent)/liter, 40.1 grams Na_2EDTA/liter, and 6 milliliters H_2NNH_2 (1 M)/liter. The plating solution and tube were placed in a water bath at 60°C. After the plating solution was depleted, the tube was removed and rinsed with deionized water at 60°C with 4 to 5 rinses.

25   Silver layers were deposited on the tube by electroless plating according to the following procedure. The tube was immersed in a plating solution at room temperature. The plating solution was composed of 0.519 grams $AgNO_3$/liter, 198 milliliters NH_4OH (28 weight percent)/liter, 40.1 grams Na_2EDTA/liter, and 6 milliliters H_2NNH_2 (1 M)/liter. The plating solution and tube were placed in a water bath at 60°C. After the plating solu-

30   tion was depleted, the tube was removed and rinsed with deionized water at 60°C with 4 to 5 rinses.

Each metallic layer was applied by contacting the tube with a plating solution for 90 minutes and was followed by rinsing the tube with deionized water, but not with inter-

mediate activation, drying or sintering. The specific layers, an estimate of the layer thicknesses, and the order of their application were Pd (about 1.5 microns), Ag (about 0.3 microns), Pd (about 1 micron), Ag (about 0.3 microns), and Pd (about 1.5 microns). (Thickness estimates were based on time of contact with the plating solutions. The average rate of

5 metal deposition was determined for a test piece of a similar support and the identical plating solution and activation procedure. The test pieces were activated, then plated for 90 minutes and then rinsed, dried and weighed. From that it was possible to estimate the thickness which was deposited over 90 minutes.)

After applying the above-described palladium/silver layers, the membrane was

10 dried at 120°C for about 48 hours. The membrane was then lightly brushed with a fine artist's paint brush. Following this, the entire plated surface of the tube was dipped in 0.1M HCl for 60 seconds at room temperature. It was then rinsed with deionized water at room temperature. Following this, the membrane was surface activated by repeating the surface activation cycle, described *supra*, three times. The membrane was then dried at 120°C

15 overnight. The membrane was then plated with another consecutive sequence of Pd/Ag/Pd/Ag/Pd layers, as described above. The membrane was subsequently dried at 120°C overnight.

The dried membrane was then lightly brushed with a fine artist's paint brush. After this brushing, the entire plated surface of the tube was dipped in 0.1M HCl for 60 seconds

20 at room temperature. It was then rinsed with deionized water at room temperature. Following this, the membrane was surface activated by repeating the surface activation cycle, described *supra*, three times. The membrane was then dried at 120°C overnight. The membrane was then plated with palladium for another 450 minutes. During this palladium plating, the plating solution was changed every 90 minutes. The membrane was rinsed

25 each time the solution was changed with deionized water at 60°C. The membrane was not surface activated between these solution changes. The resulting membrane was dried at 120°C overnight. The membrane had a total plated thickness of 14.23 microns and a high helium flux of 12.2 Nm^3/m^2-hr, indicating that the deposited layers were porous.

The surface of the deposited membrane was then abraded by hand using 600 grit

30 dry sandpaper (TUFBAK GOLD T481; Norton Abrasives, Worcester, MA). Following abrasion, the membrane was cleaned in an ultrasonic bath of isopropyl alcohol. The membrane was then dried at room temperature under flowing helium. This polishing treatment

reduced the total thickness of the membrane to 13.93 microns (determined gravimetrically). The helium flux of the membrane decreased to 10.9 Nm^3/m^2-hr.

The membrane was finished by performing 4 palladium plating cycles, each 450 minutes in duration. For each cycle the following steps were performed. First, the entire

5   plated surface of the tube was dipped in 0.1M HCl for 60 seconds at room temperature. It was then rinsed with deionized water at room temperature. Following this, the membrane was surface activated by repeating the surface activation cycle, described *supra*, three times. The membrane was then dried at 120°C overnight. Next, the membrane was plated with palladium for 450 minutes. During this palladium plating, the plating solution was

10   changed every 90 minutes. The membrane was rinsed each time the solution was changed with deionized water at 60°C. The membrane was not surface activated between these plating solution changes. The resulting membrane was dried at 120°C overnight.

Based on gravimetric data, the total palladium and silver thickness of the finished membrane was 33 microns. The membrane had a helium flux of 0.0012 Nm^3/m^2-hr. The

15   hydrogen permeance of the membrane reached a stable value of 14 Nm^3/m^2-hr over a four day test at 500°C.

The ranges and limitations provided in the instant specification and claims are those, which are believed to particularly point out and distinctly claim the instant invention. It is, however, understood that other ranges and limitations that

20   perform substantially the same function in substantially the same manner to obtain the same or substantially the same result are intended to be within the scope of the instant inventions defined by the instant specification and claims.

C L A I M S

1. A reactor, comprising:

    a)   a reaction chamber comprising:

        a catalyst bed adapted to produce reaction products comprising hydrogen gas from a hydrogen-producing feedstock; and

    b)   at least one hydrogen-selective, hydrogen-permeable gas separation module adapted to receive the reaction products from the catalyst bed and to separate the reaction products into (1) a product stream comprising hydrogen and (2) a byproduct stream, wherein the gas separation module comprises:

        (i)   a porous substrate;

        (ii)   an intermediate porous metal layer overlying the porous substrate; and

        (iii)   a hydrogen-selective membrane overlying the intermediate porous metal layer.

2. A steam reforming process for the production of hydrogen, comprising:

    (a) reacting steam with a hydrogen-producing feedstock at a temperature of from 200°C to 700°C and at a pressure of from about 0.1 MPa to about 20 MPa in a steam reforming reaction chamber containing a reforming catalyst to produce a mixture of hydrogen and carbon dioxide with a lesser amount of carbon monoxide; and

    (b) separating hydrogen from said reaction chamber and from said carbon dioxide and said carbon monoxide with a hydrogen-selective, hydrogen-permeable gas separation module, where the gas separation module comprises:

        (i)   a porous substrate;

        (ii)   an intermediate porous metal layer overlying said porous substrate; and

        (iii)   a hydrogen-selective membrane overlying the intermediate porous metal layer.

3. The reactor of claim 1 or the process of claim 2 wherein at least one distributed combustion chamber is in a heat transferring relationship with said catalyst bed.

4. The reactor or process of any of claims 1-3 wherein the gas separation module is a tube.

5. The reactor or process of any of claims 1-4 wherein a metal hydride precursor is separated from said reaction chamber by said gas separation module, where said metal hydride precursor is located to react with hydrogen permeating said gas separation module to form a metal hydride.

6. The reactor or process of any of claims 1-5 wherein the hydrogen-selective membrane is formed of palladium or an alloy thereof with at least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium; and the porous substrate is a porous ceramic substrate or a porous metal substrate selected from the group consisting of stainless steel, an alloy comprising chromium and nickel, a nickel based alloy, and an alloy comprising chromium, nickel, and molybdenum.

7. The reactor or process of any of claims 1-6 wherein the intermediate porous metal layer comprises palladium or palladium and a Group IB metal.

8. The reactor or process of any of claims 1-7 wherein the intermediate porous metal layer comprises alternating layers of palladium and a Group IB metal.

9. The reactor or process of any of claims 1-8 wherein the intermediate porous metal layer has an average thickness of from 1 micrometer to 10 micrometers.

10. The reactor or process of any of claims 1-9 wherein the mean pore size of the intermediate porous metal layer is less than the mean pore size of the porous substrate.

11. The reactor or process of any of claims 1-10 wherein a layer of a ceramic overlies the porous substrate and underlies the intermediate porous metal layer.

12. The reactor or process of any of claims 1-11 wherein the surface of the porous substrate is oxidized.

13. The reactor or process of any of claims 1-12 wherein the surface of the porous substrate is seeded with nuclei of a hydrogen-selective metal.

14. The reactor of claim 1 wherein the reactor is a steam reforming reactor and the catalyst bed is a steam reforming catalyst bed.

15. The reactor of claim 1 wherein the reactor is a dehydrogenation reactor and the catalyst bed is a dehydrogenation catalyst bed.

16. An integrated steam reforming reactor-hydrogen fuel cell comprising the reactor of claim 1 wherein the product stream containing hydrogen is delivered from the reactor to an anode compartment of a hydrogen fuel cell and the byproduct stream from the reactor is delivered to a cathode compartment of the hydrogen fuel cell.
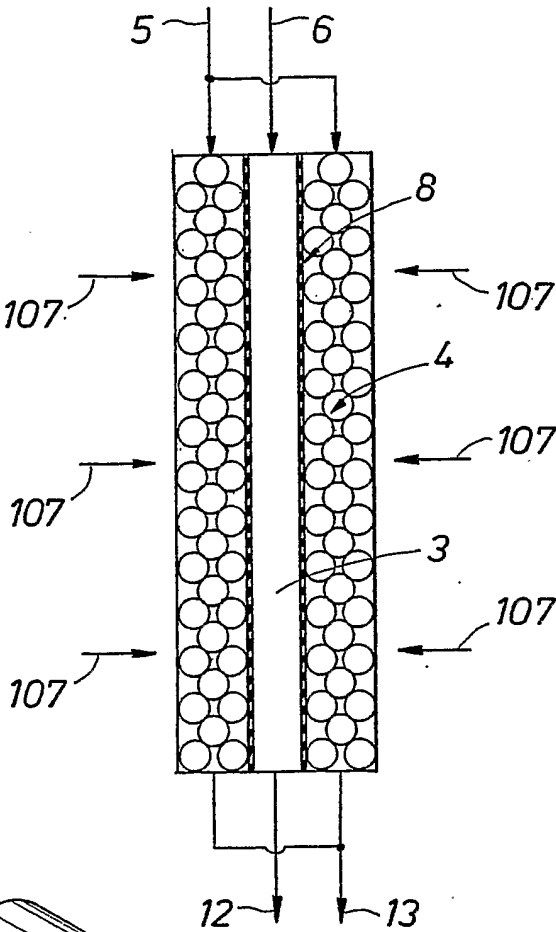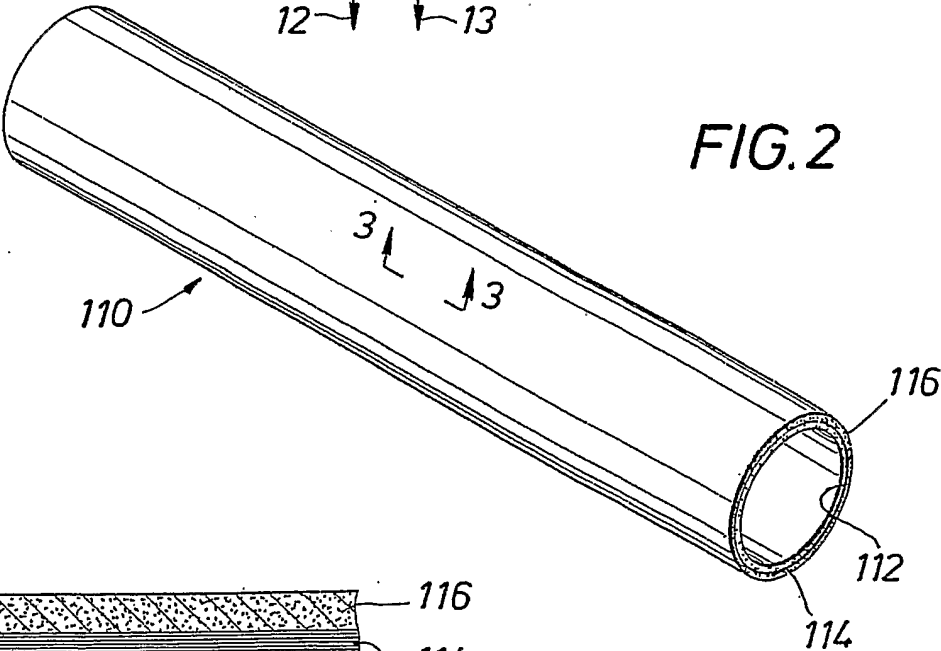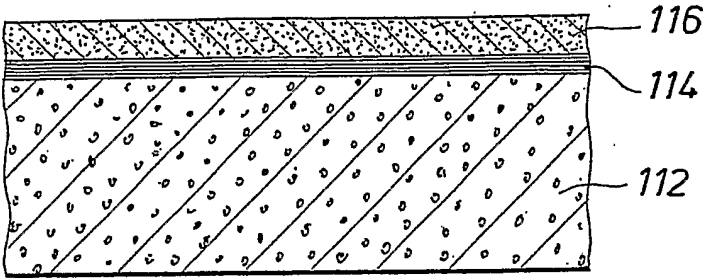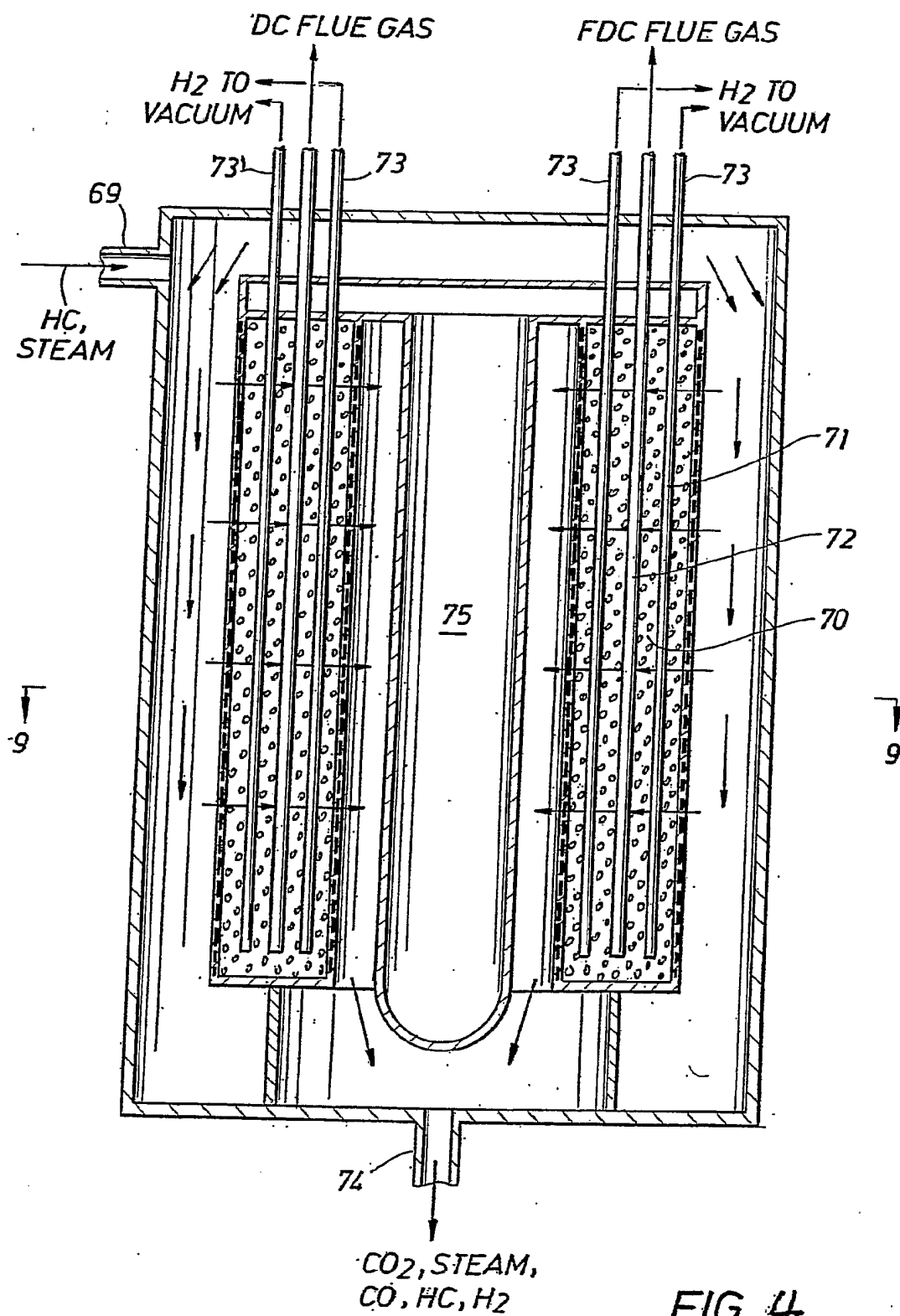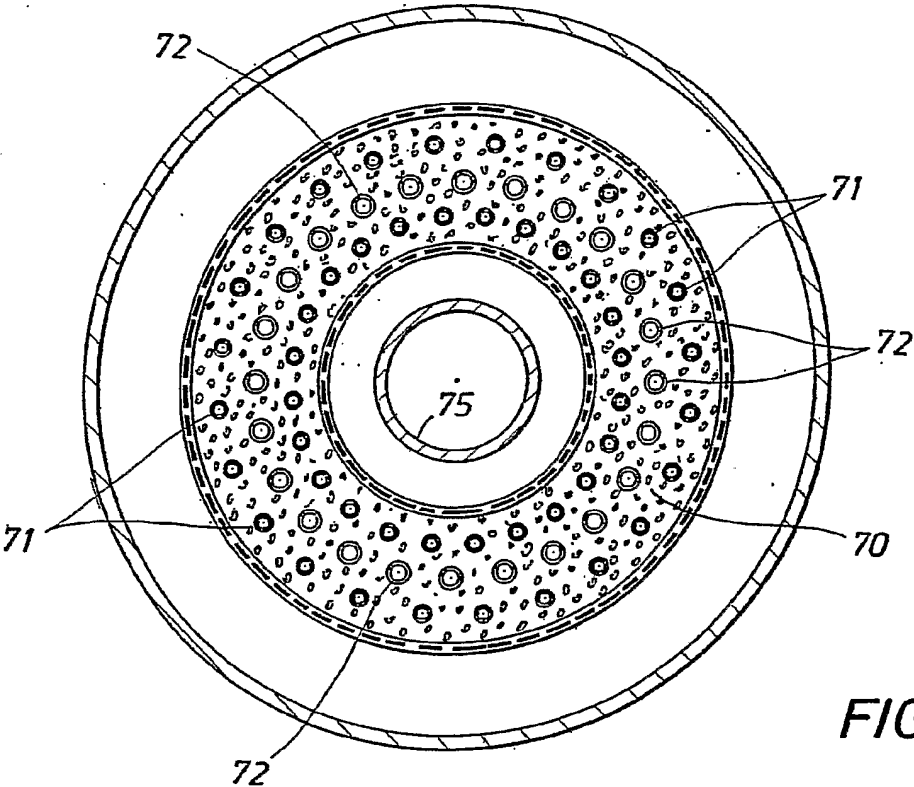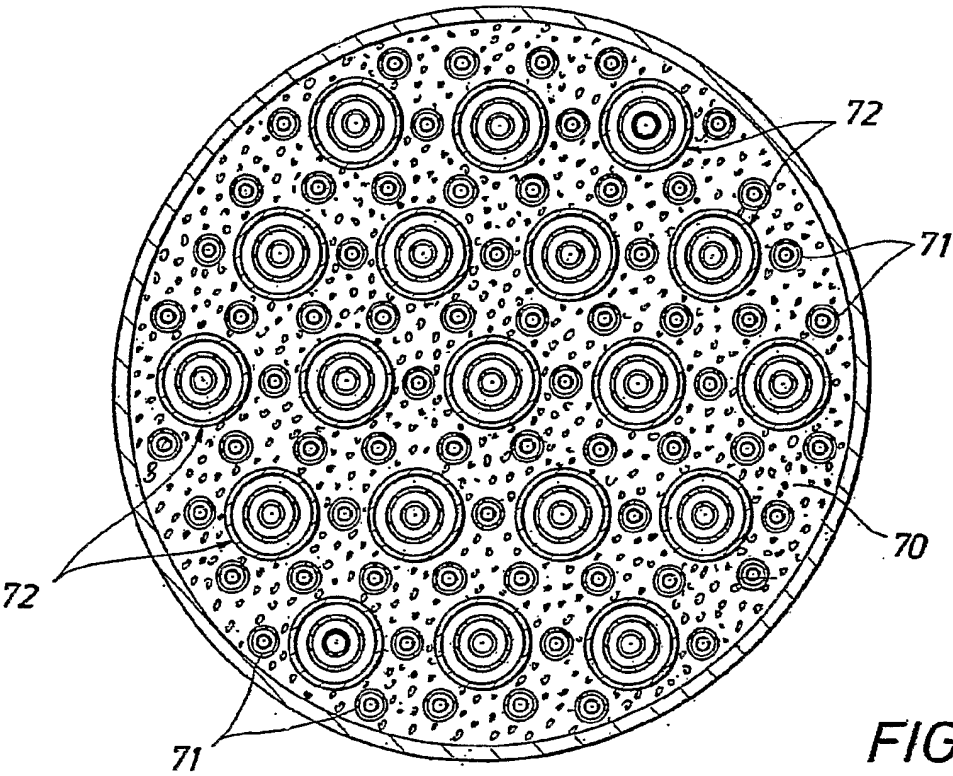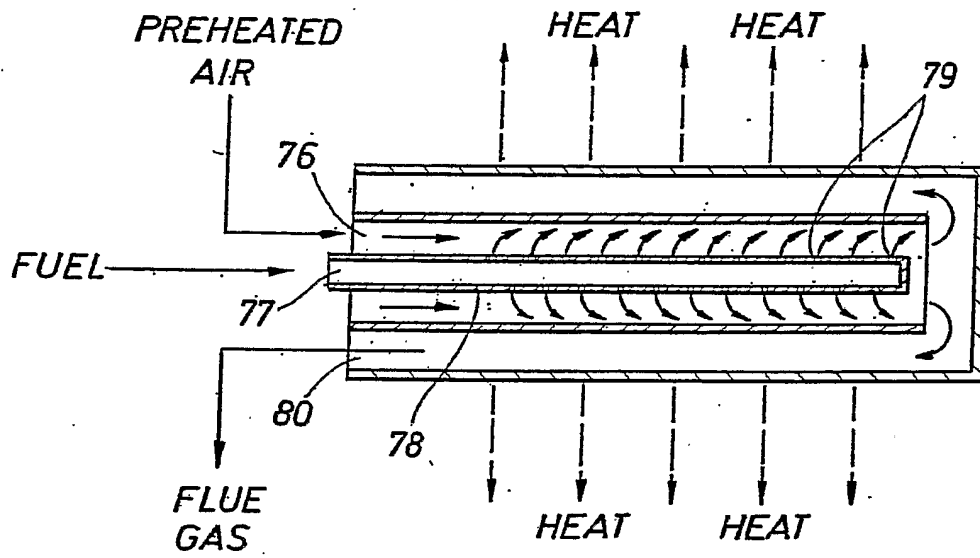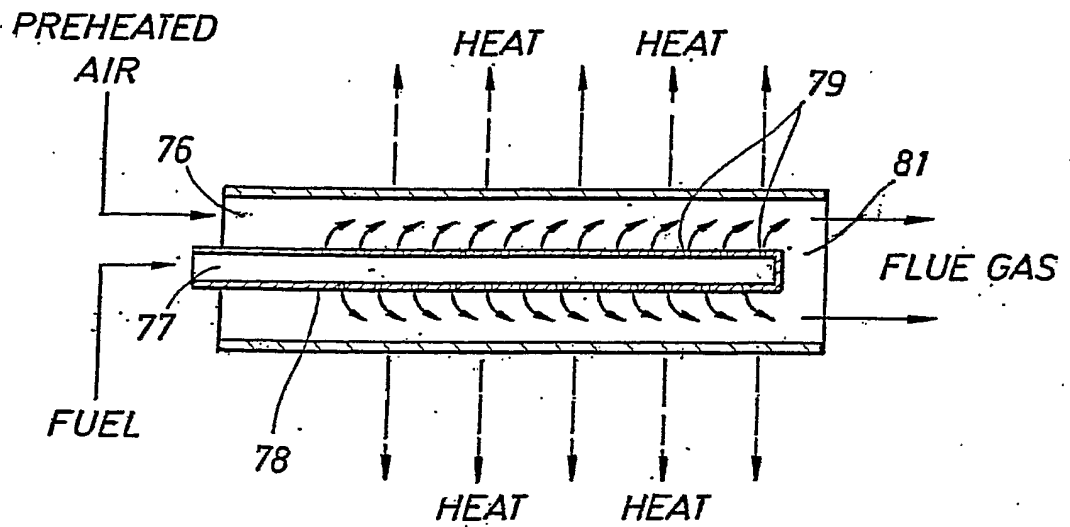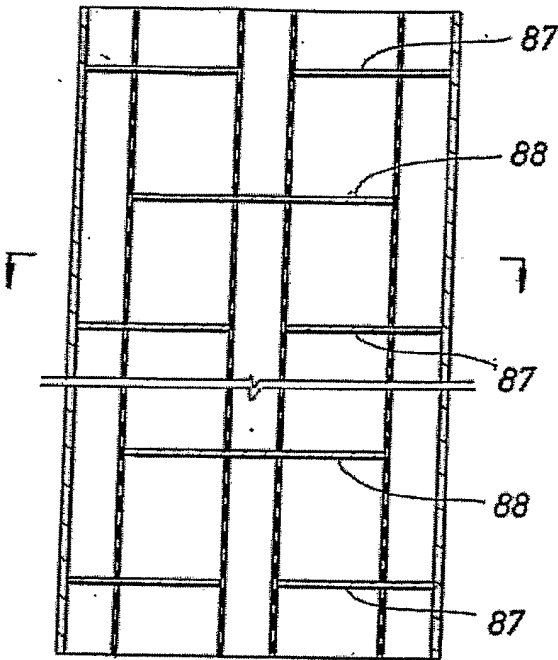
FIG.1

FIG.2
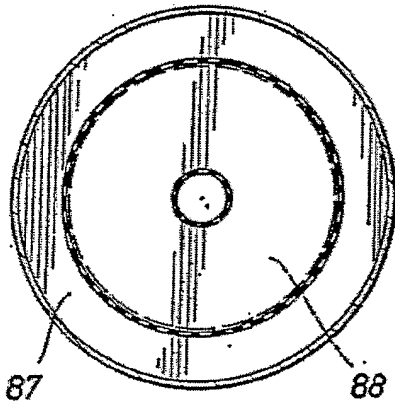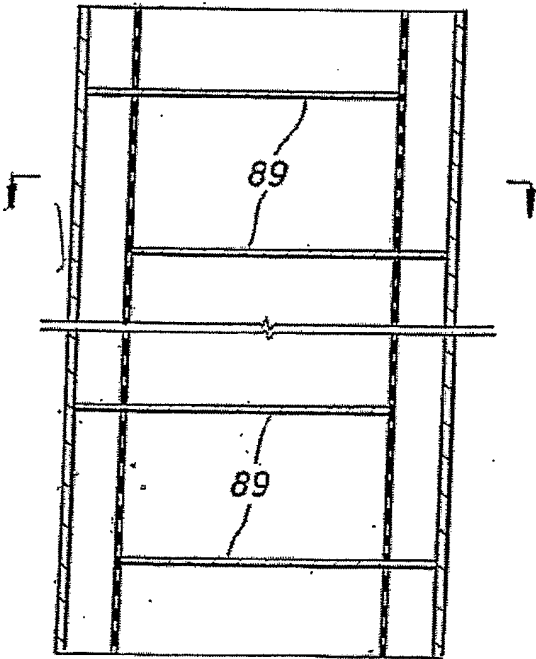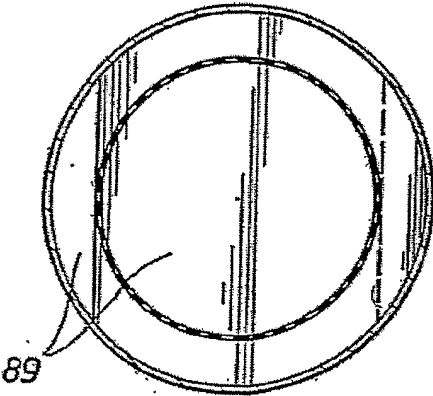
FIG.3

FIG. 4

FIG. 5

FIG. 8

FIG. 6 A

FIG. 6 B

FIG. 7
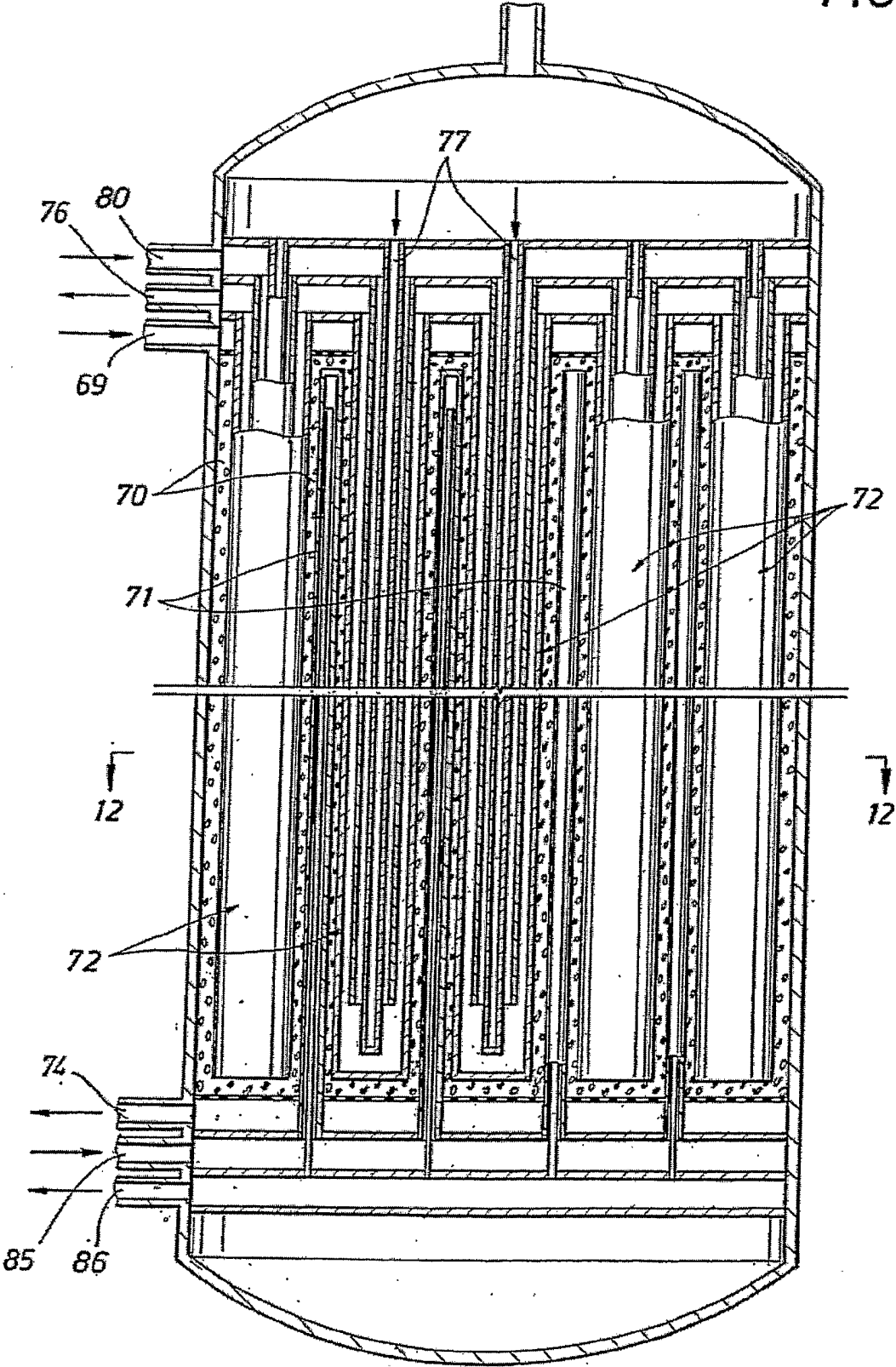
FIG. 9 A

FIG. 9 B

FIG. 9 C

FIG. 9 D

7/9

FIG. 10

FIG. 11

FIG. 12
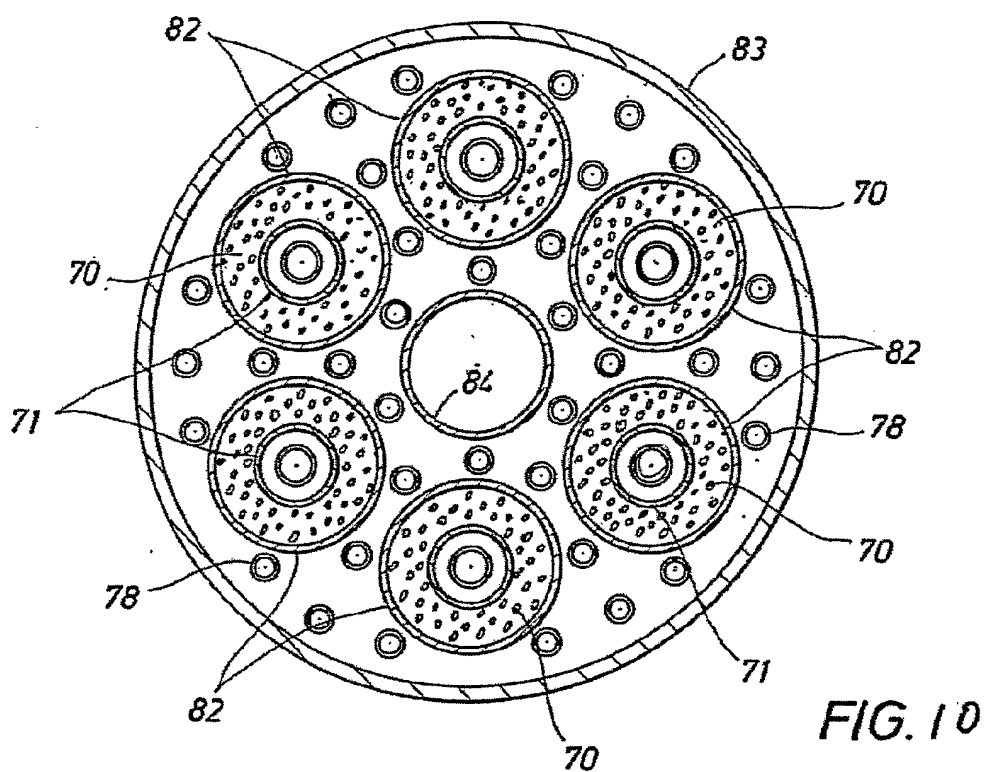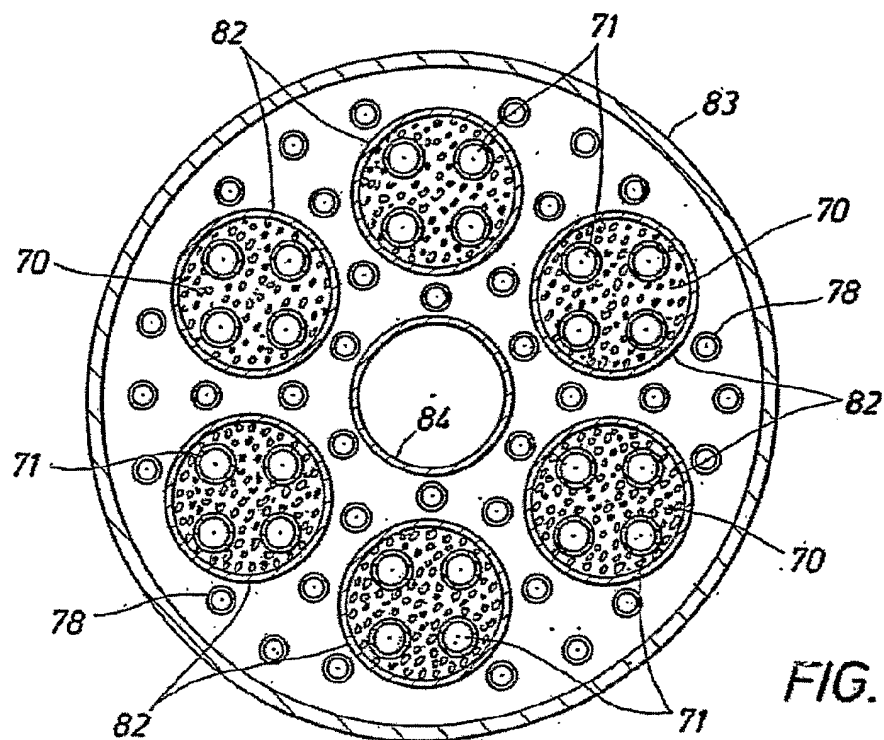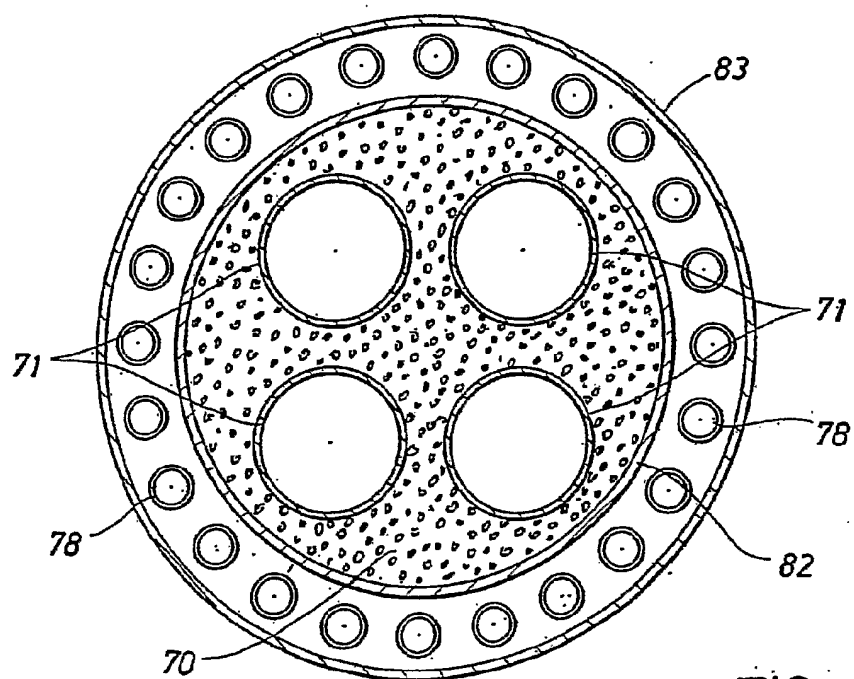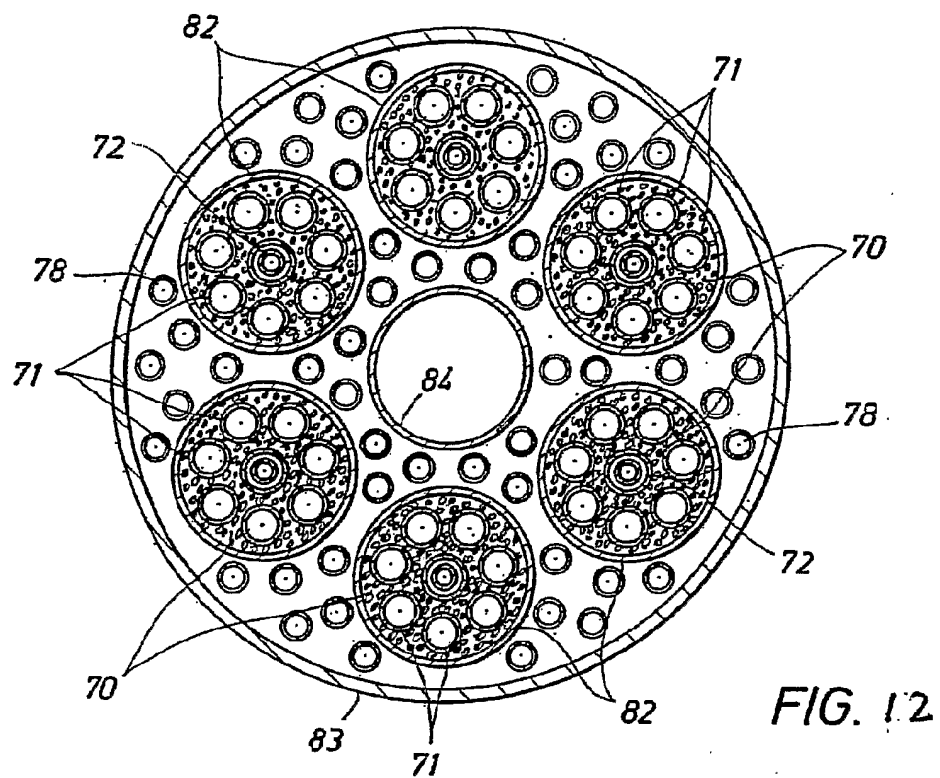
FIG. 13

FIG.14

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
B01J8/02   C01B3/50   B01D53/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B   B01J   B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/30806 A (WORCESTER POLYTECHNIC INSTITUTE) 24 June 1999 (1999-06-24) abstract page 2, line 8 - line 24 page 3, line 4 - line 11 page 3, line 15 - line 29 page 4, line 6 - line 7 page 4, line 26 - page 6, line 21; figure 1 page 8, line 20 - line 25 page 11, line 22 - line 24 claim 1 claim 26	1-16

—/—

[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 February 2006	14/02/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Thomasson, P

C(Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 498 278 A (EDLUND ET AL) 12 March 1996 (1996-03-12) abstract column 12, line 59 - column 13, line 11; figures 8a-8c examples 1,6 claims 1,7	1-16
X	US 5 217 506 A (EDLUND ET AL) 8 June 1993 (1993-06-08) abstract column 1, line 28 - line 62 figure 9 claim 1	1-16
X	US 5 393 325 A (EDLUND ET AL) 28 February 1995 (1995-02-28) abstract example 10 claim 1	1-16
X	SHU J ET AL: "Structurally stable composite Pd-Ag alloy membranes: Introduction of a diffusion barrier" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 286, no. 1, 30 September 1996 (1996-09-30), pages 72-79, XP004049419 ISSN: 0040-6090 abstract page 72 - page 73	1-16
X	EDLUND D J ET AL: "The relationship between intermetallic diffusion and flux decline in composite-metal membranes: implications for achieving long membrane lifetime" JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCIENTIFIC PUBL.COMPANY. AMSTERDAM, NL, vol. 107, no. 1, 15 November 1995 (1995-11-15), pages 147-153, XP004041247 ISSN: 0376-7388 abstract page 147 page 148; figure 1 page 153	1-16
A	WO 2004/022480 A (SHELL OIL COMPANY; MATZAKOS, ANDREAS, NICHOLAS; WELLINGTON, SCOTT, LEE) 18 March 2004 (2004-03-18) the whole document	1-16

-/--

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/066144 A (COMPAGNIE D'ETUDE DES TECHNIQUES DE L'HYDROGENE ; ETIEVANT, CLAUDE; GA) 29 August 2002 (2002-08-29) abstract page 8, line 17 - line 33; figures 1a-1c claim 1	1-16
P,X	WO 2004/098751 A (WORCESTER POLYTECHNIC INSTITUTE; MA, YI, HUA; MARDILOVICH, IVAN, P; EN) 18 November 2004 (2004-11-18) the whole document	1-16
P,X	US 2004/244590 A1 (MA YI HUA ET AL) 9 December 2004 (2004-12-09) the whole document	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9930806	A	24-06-1999	AT	234661 T	15-04-2003
			AU	1725199 A	05-07-1999
			CA	2315029 A1	24-06-1999
			DE	69812416 D1	24-04-2003
			DE	69812416 T2	08-01-2004
			EP	1042049 A1	11-10-2000
			ES	2195429 T3	01-12-2003
US 5498278	A	12-03-1996	NONE		
US 5217506	A	08-06-1993	NONE		
US 5393325	A	28-02-1995	NONE		
WO 2004022480	A	18-03-2004	AU	2003268522 A1	29-03-2004
			CA	2497441 A1	18-03-2004
			EP	1534627 A2	01-06-2005
			JP	2005538022 T	15-12-2005
WO 02066144	A	29-08-2002	CA	2438533 A1	29-08-2002
			EP	1361916 A2	19-11-2003
			FR	2820988 A1	23-08-2002
			JP	2004526559 T	02-09-2004
			US	2005072304 A1	07-04-2005
WO 2004098751	A	18-11-2004	AU	2004237778 A1	18-11-2004
			CA	2524369 A1	18-11-2004
US 2004244590	A1	09-12-2004	NONE		