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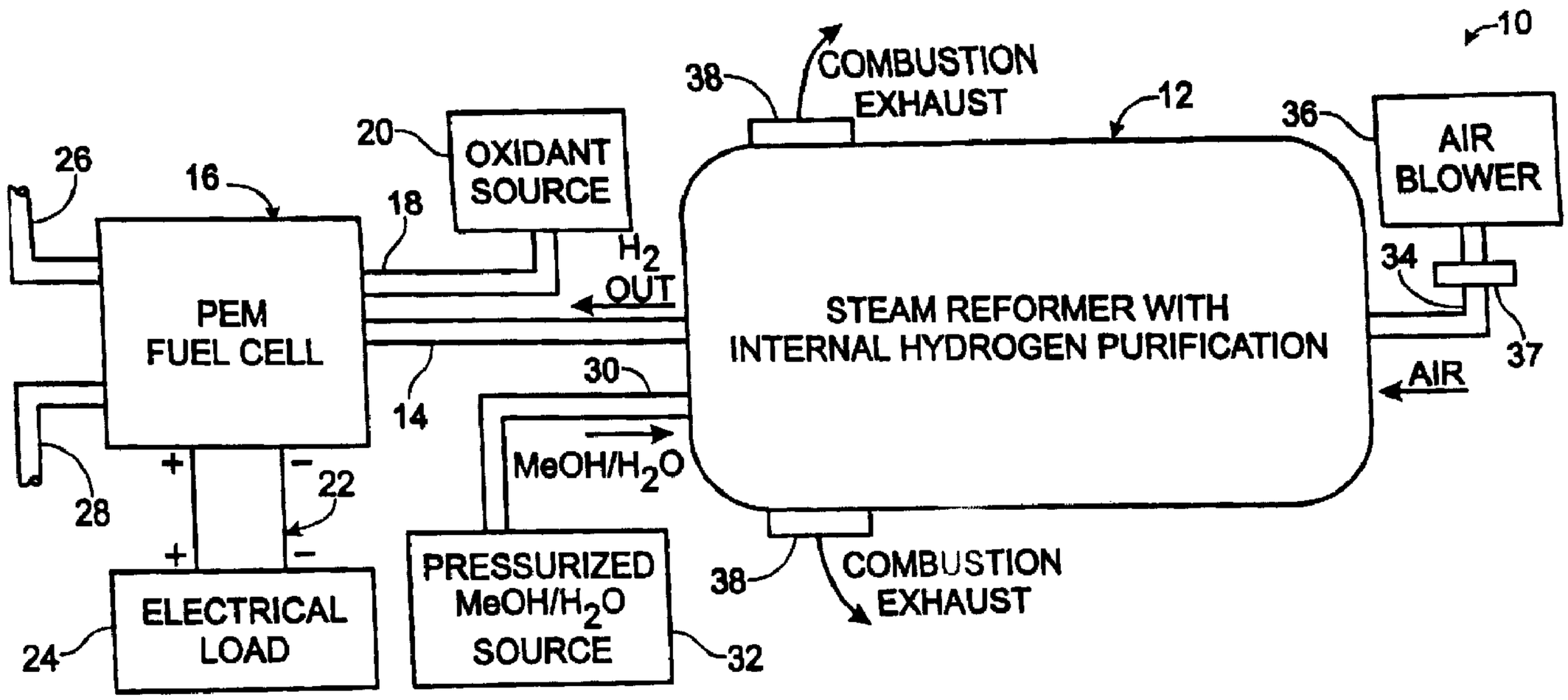


(57) Abrégé/Abstract:
A steam reformer includes a shell, a reforming region within the shell, and a hydrogen purification module. The shell has an outer surface and is adapted to receive a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol. The reforming region within the shell includes a reforming catalyst bed adapted to receive the feedstock and convert the feedstock into a reforming product stream including hydrogen, carbon monoxide and carbon dioxide. The hydrogen purification module includes a hydrogen-selective membrane in fluid communication with the reforming catalyst bed. The membrane is adapted to produce a permeate stream comprised of a portion of the reforming product stream which passes through the membrane, and a byproduct stream comprised of a portion of the reforming product stream which does not pass through the membrane. The hydrogen-selective membrane includes palladium, copper and silicon, and contains no more than 39 ppm silicon.

ABSTRACT

A steam reformer includes a shell, a reforming region within the shell, and a hydrogen purification module. The shell has an outer surface and is adapted to receive a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol. The reforming region within the shell includes a reforming catalyst bed adapted to receive the feedstock and convert the feedstock into a reforming product stream including hydrogen, carbon monoxide and carbon dioxide. The hydrogen purification module includes a hydrogen-selective membrane in fluid communication with the reforming catalyst bed. The membrane is adapted to produce a permeate stream comprised of a portion of the reforming product stream which passes through the membrane, and a byproduct stream comprised of a portion of the reforming product stream which does not pass through the membrane. The hydrogen-selective membrane includes palladium, copper and silicon, and contains no more than 39 ppm silicon.

STEAM REFORMER WITH INTERNAL HYDROGEN PURIFICATION

Background of the Invention

The present invention relates generally to energy conversion, and particularly to a process and apparatus for production of purified hydrogen by steam reforming.

Purified hydrogen is an important fuel source for many energy conversion devices. For example, fuel cells use purified hydrogen and an oxidant to produce an electrical potential. A process known as steam reforming produces by chemical reaction hydrogen and certain byproducts or impurities. A subsequent purification process removes the undesirable impurities to provide hydrogen sufficiently purified for application to a fuel cell.

Under steam reforming, one reacts steam and alcohol, (methanol or ethanol) or a hydrocarbon (such as methane or gasoline or propane), over a catalyst. Steam reforming requires elevated temperature, e.g., between 250 degrees centigrade and 800 degrees centigrade, and produces primarily hydrogen and carbon dioxide. Some trace quantities of unreacted reactants and trace quantities of byproducts such as carbon monoxide also result from steam reforming.

Trace quantities of carbon monoxide, certain concentrations of carbon dioxide, and in some cases unsaturated hydrocarbons and alcohols will poison a fuel cell. Carbon monoxide adsorbs onto the platinum catalyst of the fuel cell and inhibits operation of the fuel cell, i.e., reduces the power output of the fuel cell. To a lesser degree, carbon dioxide and other unsaturated hydrocarbons and alcohols have the same result. All impurities to some extent reduce by dilution the partial pressure of

hydrogen in the fuel cell and increase the mass transfer resistance for hydrogen to diffuse to the platinum catalyst, and thereby reduce power output of the fuel cell. Thus, fuel cells require an appropriate fuel input, i.e., purified hydrogen with no additional elements contributing to a loss in fuel cell efficiency.

Traditionally, hydrogen purification attempts to always maximize harvest of hydrogen from the reforming process. To maximize the amount of hydrogen obtained, a relatively expensive device, e.g., a thick and high quality palladium membrane, serves as a hydrogen-permeable and hydrogen-selective membrane [Ledjeff-Hey, K., V. Formanski, Th. Kalk, and J. Roes, "Compact Hydrogen Production Systems for Solid Polymer Fuel Cells" presented at the Fifth Grove Fuel Cell Symposium, September 22-25, 1997]. Such thick, high quality palladium alloy membranes support maximum harvest of hydrogen with minimal, i.e., acceptable, impurities for use in a fuel cell. Such high level of purification, however, requires significant investment in the thick, high quality palladium membrane.

Traditionally, the process of steam reforming and the subsequent process of hydrogen purification occur in separate apparatus. The advantages of combining steam reforming and hydrogen purification in a single device are known [Oertel, M., et al, "Steam Reforming of Natural Gas with Integrated Hydrogen Separation for Hydrogen Production", Chem. Eng. Technol 10 (1987) 248-255; Marianowski, L.G., and D.K. Fleming, "Hydrogen Forming Reaction Process" US Patent No. 4,810,485, March 7, 1989]. An integrated steam reforming and hydrogen purification device should provide a more compact device operating at lower temperatures not limited by the normal equilibrium limitations. Unfortunately, such a

device has yet to be reduced to practical design. Where theory in this art recognizes the advantage of combining steam reformation and hydrogen purification in a single device, the art has yet to present a practical, i.e., economical, design.

Thus, a practical integrated steam reforming and hydrogen purification device has not yet become available. The subject matter of the present invention provides a practical combined steam reforming and hydrogen purification device.

Summary of the Invention

A process for producing hydrogen containing concentrations of carbon monoxide and carbon dioxide below a given level begins by reacting an alcohol vapor (such as methanol) or a hydrocarbon vapor (such as propane) and steam to produce product hydrogen, carbon monoxide, and carbon dioxide. The reacting step occurs in the vicinity of, or immediately preceding, a hydrogen-permeable and hydrogen-selective membrane and the product hydrogen permeates the membrane. Since the membrane is likely to have holes and other defects, concentrations of the carbon monoxide and carbon dioxide above said given level also pass through the membrane. A methanation catalyst bed lies at the permeate side of the membrane and is heated whereby carbon monoxide and carbon dioxide in the methanation catalyst bed convert to methane and yield a product hydrogen stream with concentrations of carbon monoxide and carbon dioxide below said given level. Optionally, reforming catalyst may also lie at the permeate side of the membrane along with the methanation catalyst to convert to product hydrogen any unreacted alcohol or hydrocarbon feed that passes through holes or other defects in the membrane. The process concludes by withdrawing the product hydrogen from the methanation catalyst bed.

In accordance with one illustrative embodiment of the invention, there is provided a steam reformer, including a shell, a reforming region within the shell, and a hydrogen purification module. The shell has an outer surface and is adapted to receive a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol. The reforming region within the shell includes a reforming catalyst bed adapted to receive the feedstock and convert the feedstock into a reforming product stream including hydrogen, carbon monoxide and carbon dioxide. The hydrogen purification module includes a hydrogen-selective membrane in fluid communication with the reforming catalyst bed. The membrane is adapted to produce a permeate stream comprised of a portion of the reforming product stream which passes through the membrane, and a byproduct stream comprised of a portion of the reforming product stream which does not pass through the membrane. The hydrogen-selective membrane includes palladium, copper and silicon, and contains 10-39 ppm silicon.

In accordance with another illustrative embodiment, there is provided a process for producing hydrogen containing concentrations of carbon monoxide and carbon dioxide below a defined minimum level. The process includes receiving a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol, and delivering the reforming feedstock to a reforming catalyst bed to produce a reforming product stream including hydrogen, carbon monoxide and carbon dioxide. The process further includes passing the reforming product stream to a hydrogen purification module containing a hydrogen-selective membrane to produce a permeate stream including the reforming product stream which passes through the membrane, and a byproduct stream including the reforming product stream not passed through the membrane. The hydrogen-selective membrane includes palladium, copper and silicon, and the silicon is present in the membrane in a concentration of 10-39 ppm.

In accordance with another illustrative embodiment, there is provided a hydrogen purification device, including an enclosure defining an internal compartment. The enclosure includes at least one input port through which a mixed gas stream containing hydrogen gas and other gases is delivered to the enclosure, at least one product output port through which a permeate stream containing at least substantially pure hydrogen gas is removed from the enclosure, and at least one byproduct output port through which a byproduct stream containing at least a substantial portion of the other gases is removed from the enclosure.

The hydrogen purification device further includes at least one hydrogen-selective membrane within the compartment. The at least one hydrogen-selective membrane includes a first surface adapted to be contacted by the mixed gas stream, and a permeate surface generally opposed to the first surface. The permeate stream is formed from a portion of the mixed gas stream that passes through the at least one hydrogen-selective membrane to the permeate surface, and the byproduct stream is formed from a portion of the mixed gas stream that does not pass through the at least one hydrogen-selective membrane. The membrane is substantially comprised of a primary component selected from a group consisting essentially of palladium and a palladium alloy. The membrane further includes a secondary component consisting of silicon, with the silicon present in the membrane in a concentration of approximately 10-39 ppm.

In accordance with another illustrative embodiment, there is provided an improvement in a hydrogen purification device that is adapted to be operated at a temperature of at least 200° C and a pressure of at least 50 psi. The device includes an enclosure with an internal, at least substantially fluid-tight compartment having at least one inlet and at least one outlet. The compartment contains at least one hydrogen-selective metal membrane adapted to separate a mixed gas stream containing hydrogen gas and other gases into a hydrogen-rich stream containing at least substantially hydrogen gas and a byproduct stream containing at least a substantial portion of the other gases. The improvement involves the membrane being at least substantially comprised of an alloy of palladium, copper and silicon, with the silicon being present in the alloy in a concentration of 10-39 ppm.

A steam reformer according to one embodiment of the present invention includes a tubular or planar hydrogen-permeable and hydrogen selective membrane or immediately precedes the membrane. A reforming bed surrounds at least part of the membrane. An inlet to the reforming bed receives a mixture of alcohol or hydrocarbon vapor and steam and an outlet from the reforming bed releases reforming byproduct gasses. A heating element heats the reforming bed to an operating temperature and a second bed including a methanation catalyst is placed at the permeate side of the membrane. A reformer outlet withdraws hydrogen gas from the second bed. According to one aspect of the present invention, the heating element is a third bed including an oxidation catalyst surrounding at least a portion of the first bed. The reforming byproduct gasses released from the reforming bed mix with an air source and catalytically ignite to generate heat and thermally support the process of reforming within the reforming bed. In accordance with another aspect of the present invention, the reformer receives a liquid alcohol or hydrocarbon and liquid water feed and vaporizes the alcohol or hydrocarbon and water by use of heat generated in the oxidation catalyst bed. Fuels applied to the oxidation catalyst bed may include a selected amount of hydrogen allowed into the reforming byproduct gasses to support the reforming process without requiring an additional fuel source.

In accordance with another aspect of the invention, there is provided a steam reformer, including a shell, a reforming region within the shell, and a hydrogen purification module. The shell has an outer surface and is adapted to receive a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol. The reforming region within the shell includes a reforming catalyst bed adapted to receive the feedstock and convert the feedstock into a reforming product stream including hydrogen, carbon monoxide and carbon dioxide. The hydrogen purification module includes a hydrogen-selective membrane in fluid communication with the reforming catalyst bed. The membrane is adapted to produce a permeate stream comprised of a portion of the reforming product stream

which passes through the membrane, and a byproduct stream comprised of a portion of the reforming product stream which does not pass through the membrane. The hydrogen-selective membrane includes palladium, copper and oxygen, and contains no more than 29 ppm oxygen.

In accordance with another aspect of the invention, there is provided a process for producing hydrogen containing concentrations of carbon monoxide and carbon dioxide below a defined minimum level. The process includes receiving a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol, and delivering the reforming feedstock to a reforming catalyst bed to produce a reforming product stream including hydrogen, carbon monoxide and carbon dioxide. The process further includes passing the reforming product stream to a hydrogen purification module containing a hydrogen-selective membrane to produce a permeate stream comprising the reforming product stream which passes through the membrane, and a byproduct stream comprising the reforming product stream not passed through the membrane. The hydrogen-selective membrane includes palladium, copper and oxygen, and the oxygen is present in the membrane in a concentration of no more than 29 ppm.

In accordance with another aspect of the invention, there is provided a hydrogen purification device, including an enclosure defining an internal compartment. The enclosure includes at least one input port through which a mixed gas stream containing hydrogen gas and other gases is delivered to the enclosure, at least one product output port through which a permeate stream containing at least substantially pure hydrogen gas is removed from the enclosure, and at least one byproduct output port through which a byproduct stream containing at least a substantial portion of the other gases is removed from the enclosure. The hydrogen purification device further includes at least one hydrogen-selective membrane within the compartment. The at least one hydrogen-selective membrane includes a first surface adapted to be contacted by the mixed gas stream and a permeate surface generally opposed to the first surface. The permeate stream is formed from a portion of the mixed gas stream that passes

through the at least one hydrogen-selective membrane to the permeate surface, and the byproduct stream is formed from a portion of the mixed gas stream that does not pass through the at least one hydrogen-selective membrane. The membrane is substantially comprised of a primary component selected from a group consisting essentially of palladium and a palladium alloy, and the membrane further includes a secondary component consisting of oxygen, with the oxygen present in the membrane in a concentration of less than approximately 29 ppm.

In accordance with another aspect of the invention, in a hydrogen purification device that is adapted to be operated at a temperature of at least 200° C and a pressure of at least 50 psi and which includes an enclosure with an internal, at least substantially fluid-tight compartment having at least one inlet, at least one outlet, and conta2ining at least one hydrogen-selective metal membrane adapted to separate a mixed gas stream containing hydrogen gas and other gases into a hydrogen-rich stream containing at least substantially hydrogen gas and a byproduct stream containing at least a substantial portion of the other gases, there is provided an improvement, in which the membrane is at least substantially comprised of an alloy of palladium, copper and oxygen, with the oxygen being present in the alloy in a concentration of no more than
29 ppm.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation of the invention, together with further advantages and aspects thereof, may best be understood by reference to the following

description taken with the accompanying drawings wherein like reference characters refer to like elements.

Brief Description of the Drawings

For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings in which:

Fig. 1 illustrates generally an energy conversion system including a fuel cell and a steam reformer with internal hydrogen purification according to one form of the present invention.

Fig. 2 illustrates schematically a concentric, cylindrical architecture for the steam reformer with internal hydrogen purification of Fig. 1.

Fig. 3 illustrates in cross section the steam reformer with internal hydrogen purification of Fig. 1.

Fig. 4 illustrates schematically an alternate architecture for the steam reformer under the present invention nesting multiple reformer tubes within a common combustion region.

Detailed Description of the Preferred Embodiment

Fig. 1 shows an energy conversion system 10 employing a steam reformer with internal hydrogen purification (reformer) 12 according to a preferred form of the present invention. Reformer 12 provides at its outlet 14 purified hydrogen to a PEM fuel cell 16. Fuel cell 16 receives at its inlet 18 an oxidant from oxidant source 20. Fuel cell 16 produces an electrical potential 22 for application to an

electrical load 24, e.g., an electrical motor. Fuel cell 16 also includes outlets 26 and 28 serving as fuel and oxidant outlets, respectively.

For purposes of describing operation of reformer 12, the liquid feedstock will be methanol (MeOH) and water, although other alcohols or hydrocarbons may be used in place of methanol. Reformer 12 receives at its fuel inlet 30 pressurized liquid methanol and water from a pressurized methanol/water source 32. As described more fully hereafter, the pressurized mix of liquid methanol and water vaporizes within reformer 12 and reacts with a reforming catalyst to produce a hydrogen stream and a byproduct stream. A hydrogen-selective membrane separates the hydrogen stream from the byproduct stream. The hydrogen stream passes, by pressure differential, through the membrane and subsequently through a polishing catalyst to appear at the outlet 14 of reformer 12.

While traditional reforming technology allows a high percentage of hydrogen produced to be taken across a selective membrane, the process and apparatus of the present invention takes less than a maximum available amount of hydrogen across the selective membrane. The present invention thereby allows use of a lesser-grade and, therefore, less expensive selective membrane. In addition, because less than the maximum amount of hydrogen is separated as a product stream, the required membrane area is reduced under this aspect of the present invention. The remaining portion of hydrogen enters the byproduct stream, mixes with air provided at inlet 34 by air blower 36, and reacts with a combustion catalyst within reformer 12 to support elevated temperatures needed for steam reforming within reformer 12. Reformer 12 thereby uses the byproduct stream, including a selected amount of

hydrogen remaining therein, as a fuel source for its combustion process. No additional fuel source is applied to reformer 12 to support combustion. Reformer 12 also includes a plurality of combustion exhaust ports 38 releasing combustion byproducts.

The optimum amount of hydrogen to recover as a product stream is calculated from the heating value (enthalpy of combustion) of hydrogen. Sufficient hydrogen must be supplied in the byproduct stream to the catalytic combustion region so that the heat of combustion exceeds the total heat requirement of the reformer. The total heat requirement of the reformer (ΔH_{total}) is given by

$$\Delta H_{total} = \Delta H_{rxn} + \Delta H_{vap} + \Delta H_{cp} + \Delta H_{loss}$$

where ΔH_{rxn} is the enthalpy of the reforming reactions; ΔH_{vap} is the enthalpy of vaporization of the liquid feed stock; ΔH_{cp} is the enthalpy required to heat the vaporized feed stock to the reforming temperature; and ΔH_{loss} is the heat lost to the surrounding environment. Heat loss from the reformer is minimized (and reduced to a negligible degree) with adequate insulation.

In the case of steam reforming methanol according to the following reaction stoichiometry

$$CH_3OH + H_2O = CO_2 + 3H_2$$

where 8.4 gmole methanol and 8.4 gmole water are required to yield sufficient hydrogen (21 std. ft^3) to generate about 1 kW_e. Assuming no heat loss and no heat exchange (between discharged hot streams and the relatively cold feed stock stream) ΔH_{total} is 300 kcal. Since the heat of combustion for hydrogen is 57.8 kcal/gmole, approximately 5.2 gmoles of hydrogen (4.3 std.ft^3) must be combusted to provide the required 300 kcal of heat for steam reforming sufficient methanol to generate 1kW_e.

So, 70% to 80% of the hydrogen produced in the reformer is recovered as a product stream and the remaining 20% to 30% of the hydrogen is passed to the catalytic combustor in the byproduct stream to provide a fuel stream with sufficient heating value to meet the heating requirements (ΔH_{total}) of the reformer.

Fig. 2 illustrates schematically the concentric cylindrical architecture of steam reformer 12. In Fig. 2, reformer 12 includes in concentric relation an outermost metal tube 50, an inner metal tube 52, a hydrogen-selective membrane tube 54, and an innermost metal tube 56. Tubes 50, 52, 54, and 56 are of successively smaller diameter and arranged in concentric relation to one another. An annular combustion region 60 exists in the space within tube 50 but external of tube 52. An annular reforming region 62 exists within tube 52 but external of membrane tube 54. An annular hydrogen transport region 64 exists within membrane tube 54, but external of tube 56. A cylindrical polishing region 66 resides within the metal tube 56.

Fig. 3 illustrates in cross section the steam reformer 12. In Fig. 3, outermost metal tube 50, a generally closed-end tubular structure, receives at one end via inlet 34 an air supply and releases at combustion ports 38 combustion byproducts. Within combustion region 60, a combustion catalyst 100 resides near air inlet 34. Alternatively, combustion catalyst 100 may be arranged as a plurality of bands spaced at intervals within combustion region 60. Suitable combustion catalyst materials include platinum supported on alumina or other inert and thermally-stable ceramic. Inlet 30, carrying the pressurized mix of methanol and water, passes through the end wall 50a of tube 50 and forms a coil 30a wrapping about the innermost metal tube 56 within the combustion region 60, although metal tube 56 need not necessarily pass

through the axis of coil 30a. The distal end of coil 30a passes through the closed end 52a of tube 52 and opens into the reforming region 62. The pressurized mix of liquid methanol and water entering coil 30a vaporizes at the elevated temperatures of combustion region 60 and enters the reforming region 62 as vapor.

Within reforming region 62 a reforming catalyst 102 (e.g., BASF catalyst K3-110 or ICI catalyst 52-8) reacts with the vaporized mix of methanol and water to produce hydrogen in the vicinity of the membrane tube 54. Membrane tube 54 is composed of one of a variety of hydrogen-permeable and hydrogen-selective materials including ceramics, carbon, and metals. Especially preferred materials for fabricating said membrane tube 54 are hydrogen-permeable palladium alloys, e.g., palladium alloyed with 35-45 wt% silver. Each end of membrane tube 54 is sealed by a metal cap 104. A metal gauze 106 within the reforming region 62 surrounds each cap 104 and maintains the catalyst 102 within region 62 and in the vicinity of membrane tube 54. A hydrogen stream 103 migrates by pressure differential through membrane tube 54 and into hydrogen transport region 64. A thin membrane tube 54 requires support against deformation under the pressure differential between reforming region 62 and hydrogen transport region 64. For this purpose, a tension spring 101 supports membrane tube 54 from within while allowing hydrogen stream 103 to pass by, into and along transport region 64.

Because a thin palladium alloy membrane may be used under the present invention, special construction methods have been developed under the present invention to make use of a delicate structure such as thin membrane tube 54. Under conventional practice, a thick palladium alloy membrane can be brazed because it can withstand the high

temperatures and liquid phase aspects of brazing. A thin palladium alloy membrane, as proposed herein however, cannot be brazed under conventional methods because the elevated temperature and liquid brazing alloy destroy such thin palladium material. A thin membrane tube 54 could, under conventional practice for example, attach to end caps 104 and establish a gas-tight seal by use of gaskets and suitable support structures. As discussed more fully hereafter, under the present invention a thin palladium alloy membrane, e.g., tube 54, attaches to end caps 104 by first attaching a foil (not shown in Fig. 3), e.g., a copper or nickel foil, to the ends of tube 54 by ultrasonic welding and then brazing the foil-wrapped ends of tube 54 to end caps 104.

Hydrogen stream 103 travels within transport region 64 toward and into the open end 56a of tube 56. Hydrogen stream 103 includes some impurities, e.g., carbon monoxide, carbon dioxide and unreacted methanol and water vapor, also traveling along transport region 64 and into innermost tube 56 at its open end 56a. All of hydrogen stream 103 enters the open end 56a of innermost tube 56.

Within tube 56 a polishing catalyst 110 reacts with impurities in the hydrogen stream 103 passing therethrough. Metal gauze 112 downstream from catalyst 110 holds catalyst 110 within tube 56. Polishing catalyst 110 (e.g., BASF catalyst G1-80 or ICI catalyst 23-1) reacts with certain impurities remaining in hydrogen stream 103, e.g., as much as 1% of carbon monoxide and carbon dioxide, and converts such impurities to innocuous byproducts, e.g., methane. Stream 103 of purified hydrogen and, now innocuous, byproducts passes through metal gauze 112 and exits reformer 12 at the outlet 14, i.e., at the opposite end 56b of tube 56.

Polishing catalyst 110 may be several separate catalysts within tube 56. In order to deal with carbon monoxide and carbon dioxide impurities, one uses a methanation catalyst. The process of methanation, i.e., reacting carbon monoxide or carbon dioxide with hydrogen to yield methane as shown below, is well known.

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

$$CO + 3H_2 = CH_4 + H_2O$$

Methanation provides an acceptable polishing step because methane is considered relatively inert or innocuous to the fuel cell 16 (Fig. 1) whereas carbon dioxide and carbon monoxide are poisonous to the fuel cell.

If reformer 12 uses methanol in the steam reforming step, and leaks in the membrane tube 54 allow carbon monoxide and carbon dioxide to pass into the hydrogen stream 103, some unreacted methanol and water vapor may exist in the hydrogen stream 103. To convert such unreacted methanol into a harmless byproduct prior to entering the fuel cell 16 (Fig. 1), a reforming catalyst which is a low temperature copper/zinc shift catalyst, is placed through a portion (e.g., one-fourth to one-third) of the polishing catalyst bed, i.e., innermost tube 56, followed downstream by a methanation catalyst.

The predominant chemical reaction for steam reforming methanol is shown below.

$$CH_3OH + H_2O = CO_2 + 3H_2$$

Returning to reforming region 62, steam reforming byproduct stream 105 moves toward closed end 52b of tube 52 and through critical orifice 120 serving as an outlet for tube 52 and discharging near air inlet 34. Optionally, deflector 57

directs the flow of byproduct stream 105 and air from inlet 34 toward combustion catalyst 100. Byproduct stream 105 thereby encounters and mixes with the air inflow 107 of air at inlet 34. Air inflow 107 may be preheated to enhance the catalytic ignition within combustion region 60. For example, an air heater 37 (Fig. 1) may be provided in series along the inlet 34 to reformer 12. Alternatively, inlet 34 may be routed through combustion region 60 as shown schematically in Fig. 3. The resulting mixture travels toward and through combustion catalyst 100 and ignites thereat. The combustion byproducts then travel through combustion region 60 and eventually, after heating coil 30a and thermally supporting the steam reforming process within region 62, exit reformer 12 at the combustion exhaust ports 38.

Reformer 12 operates at a relatively lower temperature than conventional steam reforming devices. Because reformer 12 continually purifies hydrogen as it is produced, the steam reforming reaction may be conducted well away from its equilibrium limitation. Although equilibrium limitations are generally not important in the case of steam reforming methanol, they are very important in the case of steam reforming methane (natural gas). Unreacted reactants in the relatively lower temperature reforming process tend to be eventually reacted due to the continuous siphoning of hydrogen from the process. Under the present invention, the steam reforming process may be operated at approximately 250 to 600 degrees Celsius. For methanol reforming the operating temperature of the reformer would be approximately 250 to 300 degrees Celsius.

To create an appropriate pressure differential at membrane tube 54, the liquid methanol and water should be pumped, i.e., provided by source 32, at

approximately 6 to 20 atmospheres. The polishing step should be conducted at approximately one to three atmospheres within polishing region 66. The pressure within hydrogen transport region 64 is essentially equal to the pressure within polishing region 66. The reforming process should be operated at 6 to 20 atmospheres to provide a substantial pressure differential across membrane tube 54. Critical flow orifice 120 can be sized to provide a pressure drop from the reforming region 62 (6 to 20 atmospheres) to one atmosphere within the combustion region 60. The byproduct stream 105 thereby enters the combustion region 60 at approximately one atmosphere. This allows operation of the air supply at inlet 34 at approximately one atmosphere, and thereby allows use of an inexpensive air blower 36.

Dimensions for reformer 12 sufficient to feed a typical fuel cell 16 are relatively small. Ten liters per minute (21 cubic feet per hour) of hydrogen is sufficient to generate one kilowatt of electrical energy in fuel cell 16. A steam reformer 12 under the present invention sufficient to support a one kilowatt fuel cell 16 would be roughly three inches in diameter by 15 to 16 inches in length. To increase volumetric production, the length of reformer 12 could be increased or the diameter of reformer 12 could be increased. The volumetric production rate for reformer 12 is limited primarily by the area of membrane 56 exposed to the reforming process. Increasing the length of reformer 12 or the diameter of reformer 12 increases the exposed area of membrane tube 54 and thereby increases hydrogen output for reformer 12. However, multiple standard-sized reformers 12 may be employed in parallel within a common combustion zone.

Fig. 4 illustrates schematically the architecture of an alternate reformer 12' with an enlarged outermost metal tube 50' defining a common combustion region 60'. Within the relatively larger combustion region 60', a plurality of reformer tubes 51, i.e., each a combination of a tube 52, a tube 54, and a tube 56, are arranged in spaced relation. While not shown in Fig. 4 for purposes of clarity, reformer 12' would include a feedstock inlet, a product hydrogen outlet, and a combustion gas outlet. A common air inlet 34 supplies air to the common combustion region 60'. As may be appreciated, each of reformer tubes 51 provides a byproduct stream 105 (not shown in Fig. 4) to the common combustion region 60'.

Returning to Fig. 3, reformer 12 must be initiated to operate. Generally, the reforming region 62 must be elevated to approximately 150 to 200 degrees Celsius if methanol is the feedstock, or 300 to 500 degrees Celsius if hydrocarbons are the feedstock. Once the reforming process begins, the byproduct stream 105, including by design a given amount of hydrogen as combustion fuel, enters the combustion region 60, encounters combustion catalyst 100, and combusts to thermally support the steam reforming process. The combustion catalyst only needs hydrogen present (mixed with air) to ignite the byproduct stream 105. The goal in starting reformer 12, therefore, is to elevate the reforming region 62 to approximately 150 to 200 degrees Celsius (in the case of methanol reforming).

A simple cartridge-type electric resistance heater 140, either inserted into the reforming catalyst 102 or, as illustrated in Fig. 3, into the center of tube 56 initiates operation of reformer 12. Alternatively, a resistance heater may be used to heat the methanol and water feed provided at inlet 30. In either event, once the

reforming catalyst 102 reaches a sufficiently high temperature (150 to 200 degrees Celsius) the reforming reaction begins and the combustion catalyst 100 reacts with hydrogen present in byproduct stream 105. At this point, the electrical resistance heater 140 can be shut down. A 50 to 100 watt resistance heater 140 should be adequate, based on conventional thermal mass calculations, to sufficiently heat the reforming region 62 in a matter of minutes.

An alternate form of the present invention is a reformer with its combustion system distributed through the reformation region to improve heat transfer from the combustion process to the reformation process. A first alternate reformer is a steam reformer with internal hydrogen purification receiving at its inlet a feed stock, e.g., methanol and water, and providing at its outlet purified hydrogen for application to, for example, a fuel cell. As with earlier embodiments of the present invention, the reformer leaves a selected portion of hydrogen in its byproduct stream to support the combustion process. Combustion byproducts exit at the exhaust port.

The reformer includes an outer metal tube sealed at each end by end plates and gaskets. Bolts secure the end plates against the shoulders at each end of the tube. A hydrogen purification module lies within and generally concentric to the outer metal tube and includes a thin palladium alloy membrane tube sealed by end caps. Alternatively, the membrane tube may be comprised of hydrogen-selective and hydrogen-permeable materials other than palladium alloys, including porous carbon, porous ceramics, hydrogen-permeable metals other than palladium, porous metals, and metal-coated porous carbon and porous ceramics and porous metals. As may be appreciated, the membrane tube and the caps may be supported in some fashion within the outer metal tube. One of the end caps communicates with the outlet through one of the end plates and the

product hydrogen stream emerges from the outlet port. A polishing catalyst bed, preferably a methanation catalyst, is located at the permeate side of the membrane tube as discussed earlier and shown in Fig. 3.

The inlet passes through the end plate wall and couples to a vaporization coil. An outlet of the coil feeds directly into the reformation region defined as being within the outer metal tube but external of the membrane tube. Also located within and distributed throughout the reformation region is a combustion coil. For example, in a particular embodiment, the coil surrounds in spiral fashion the membrane tube and extends substantially throughout the entire reformation region. A combustion catalyst lies within and either along the length of the coil or localized within the coil at or near its end. The end of the coil receives a fuel stock, as described more fully hereafter, and combustion occurs within the coil as the fuel stock travels along the coil and encounters the combustion catalyst therein. Because the coil extends uniformly throughout the reformation region and because the coil provides significant surface area, rapid and well distributed heat transfer occurs from the combustion process occurring within the coil to the surrounding reformation region.

The reformation region couples through the wall of one end plate at its outlet to a conduit. The conduit carries the byproduct stream, i.e., the byproduct of hydrogen reformation including a selected amount of hydrogen intentionally not taken across the membrane tube, to the combustion process. The conduit delivers the byproduct stream to a pressure let down valve. The byproduct stream then continues, at lowered pressure, into an intake manifold. The manifold includes an air inlet, e.g., coupled to an air blower or to discharged air from the cathode component of the fuel cell, and an air passage way carrying combustion air to a mixing region at or near the inlet of the combustion coil.

The combustion fuel stock as provided by the byproduct stream, thereby mixes with the incoming combustion air in the mixing region and enters the inlet end of the combustion coil. A combustion catalyst within the coil ignites the fuel stream and heat transfers efficiently and rapidly in well distributed fashion into and throughout the reformation region.

While a coil or spiral form of combustion system has been described, i.e., the combustion coil, other shapes may be employed as a combustion system within the reformation region. For example, generally tubular structures may assume a variety of forms for distribution throughout the reformation region. As discussed more fully hereafter, a counter-current combustion system establishes improved, i.e., uniform, heat distribution throughout the reformation region. Thus, the advantage of distributing a combustion system throughout the reformation region may be achieved in a variety of specific configurations.

In steam reformer 12 (Fig. 3), the combustion process occurred in a region surrounding the reformation region, i.e., externally of the tube 52 (Fig. 3) thereby requiring heat transfer into and across metal tube 52. From the inner surface of tube 52, heat transfer then occurred by migration across the reformation region. In the first alternate steam reformer discussed above, however, heat generated within and distributed throughout the reformation region, i.e., within the coil, better transfers more rapidly throughout the reformation region. In essence, the combustion process has been brought into and distributed throughout the reformation region. Heat transfer improves because the flow of reformation gasses passes directly over and around the coil. Generally, the coil provides significantly greater surface area for heat transfer between combustion and reformation as compared to the surface area provided

by tube 52 in reformer 12. Heat energy need not transfer into and migrate across the reformation region, but rather generates within the reformation region and radiates outward throughout the reformation region.

In another embodiment of the present invention, the reformer not only distributes combustion heat energy throughout the reformation region, but also provides the advantage of isolating the vaporization process from the reformation process. Generally, a preferred temperature for vaporization of the feed stock, e.g., 400-650 degrees Centigrade, is greater than a preferred temperature, e.g., 250-500 degrees Centigrade, for hydrogen reformation. A second alternate steam reformer includes an outer metal tube defining therein a reformation region. The outer metal tube includes shoulders at each end. A vaporization module attaches to the shoulders at one end of the outer metal tube. The module defines a vaporization chamber isolated relative to the reformation region. More particularly, the module includes a generally cylindrical barrel having an open end and a closed end. An end plate and a gasket seal the vaporization chamber, i.e., close the otherwise open end of the barrel. The closed end of the barrel couples to the shoulders of the outer metal tube. In this manner, the closed end together with a gasket seal the end of the outer metal tube and, thereby, seal the reformation chamber. By isolating the vaporization chamber and the reformation chamber, vaporization occurs at preferred, i.e., significantly higher, temperatures than temperatures preferred for the reformation chamber.

An inlet passes through the end plate and feeds into the vaporization coil as located within the vaporization chamber. The distal end of the vaporization coil then passes through the closed end of the barrel and feeds into the reformation chamber. In this manner, vaporized feed stock, i.e.,

methanol and water vapor, enter the reformation region and chemically interact with a reformation catalyst distributed throughout the reformation region.

The vaporization chamber includes outlets passing combustion exhaust along corresponding conduits extending through the combustion region. In this manner, the heat energy of the combustion exhaust transfers through the conduits and into the reformation region. Again, distributing heat energy throughout and within the reformation region improves heat transfer distribution and rate. For example, the vaporization chamber includes outlets passing combustion gas into corresponding conduits. The combustion exhaust remains isolated relative to the combustion region, but the heat energy of the combustion exhaust migrates through the conduits and into the combustion region. The conduits pass through an end plate, secured to the shoulders at an end of the outer metal tube, and the combustion exhaust releases to atmosphere. Heat transfer can be improved, and the degree of resistance to flow and turbulence along the exterior conduits can be controlled by use of baffles.

As in previously described embodiments, reformation occurring in the reformation region supports migration of hydrogen across a tubular palladium alloy membrane. Other hydrogen-permeable and hydrogen-selective compositions that may be used in place of palladium alloys for the membrane include porous carbon, porous ceramic, hydrogen-permeable metals, porous metals, and metal-coated porous ceramics and porous carbon and porous metal. The tubular membrane, sealed at each end by means of end caps, feeds the product hydrogen stream at the outlet of the second alternate reformer. A polishing catalyst bed (not shown) is located at the permeate side of the tubular membrane as shown in Fig. 3. A preferred polishing catalyst is a methanation catalyst.

By intentionally not recovering all hydrogen available in the reformation region, the remaining hydrogen sweeps away in the byproduct stream and provides a fuel stock for the vaporization module. More particularly, the reformation region couples to a conduit passing through an end plate. The conduit carries the byproduct stream, including a selected amount of hydrogen remaining therein as fuel stock. The conduit passes through a pressure let down valve and provides the reduced-pressure fuel stock flow to an inlet manifold. The inlet manifold operates in similar fashion to the inlet manifold of the first alternate reformer, i.e., receiving combustion air and promoting mixing of the combustion air and the reduced-pressure byproduct stream. As the combined combustion air and stream intermix at the mixing region, an igniter triggers combustion thereof. The igniter may be a variety of devices, e.g., glow plug, spark plug, catalyst, and the like. In the preferred form of the second alternate reformer, however, a high voltage spark ignition or possibly a glow plug is considered preferred as igniter for long term reliability and ease of replacement.

In addition to isolation of vaporization, the second alternate reformer also provides the advantage of a preferred low pressure drop between the initiation of combustion and exhaust from the combustion region. The architecture of the second alternate reformer provides a lower pressure combustion process because its conduits are generally straight conduits offering reduced and controlled resistance to the flow of combustion exhaust gasses. With a lower pressure combustion process, combustion air, e.g., such as is provided at an inlet of the intake manifold, may be provided by a relatively lower pressure and relatively less expensive air blower.

An alternate combustion system applicable to the various embodiments of the present invention is a double-walled counter current combustor that includes an inlet manifold receiving a byproduct stream and an air stream. The byproduct stream is taken from a reformation process as a byproduct, but includes a selected amount of hydrogen intentionally left therein as a fuel stock for combustion. The byproduct stream travels along an inner conduit and exits the conduit in an inner mixing region. The air stream travels along the inlet manifold, generally surrounding and parallel to the inner conduit and encounters the byproduct stream in the mixing region. The mixing region comprises an inner tube carrying therealong the mixture of combustion air, i.e., the air stream and fuel gas, i.e., the byproduct stream. The inner tube is closed at one end, i.e., an end forming a portion of the inlet manifold. The open end of the inner tube, however, releases mixed fuel gas and combustion air into an outer mixing region. The outer mixing region is defined by an outer tube. The outer tube is closed at each of its ends with the inlet manifold passing through one end. A combustion catalyst is distributed throughout the inner and outer mixing regions. Alternately, the combustion catalyst may be localized within the inner tube at or near the inner mixing region.

The highest temperature combustion occurs when the mixture of fuel gas and combustion air first encounter the combustion catalyst, i.e., at the outlet of the inlet manifold. As the gas mixture continues along the inner tube and encounters the catalyst therealong, continued combustion occurs but generally at progressively lower temperatures. As the gas mixture continues out of the inner tube, at its open end, it reverses direction and travels back along the outer tube and encounters more of the catalyst. As a result, heat energy is

produced along the length of the inner and outer tubes and exhaust gases exit at the exhaust port.

Generally, a significant temperature gradient exists along a combustion catalyst bed, the hottest portion being where the fuel gas and combustion air first encounter the combustion catalyst or igniter device. Such significant temperature gradient can be undesirable, especially when applying the heat energy to a reformation process most desirably conducted at uniform temperature throughout. Under the present invention, the double-walled counter current combustor provides a more uniform temperature gradient along its length as compared to a conventional combustion bed. The hottest gasses within this combustor, i.e., near the inlet manifold, release heat energy through the inner tube and into the coolest gasses within the combustor, i.e., near the exhaust port. By thermally coupling the hottest portion of the gasses with the coolest portion of the gasses a more uniform overall temperature gradient exists along the combustor.

There is a relationship between the length L of a combustion bed (x axis) and temperature T therealong (y axis). In a conventional combustion bed, there are substantially higher temperatures at the beginning of the combustion bed followed by a significant drop in temperature throughout the conventional combustion bed. With the double-walled, counter current combustor, however, a more uniform, i.e., more flat, temperature gradient is obtained. More particularly, this combustor provides a shallow and fairly level curve indicating a uniform temperature along the length of the combustor. Accordingly, this combustor provides a more uniform dispersal of heat energy into a reformation region.

It will be understood that the double-walled architecture of the combustion device may be formed as a generally straight device, or it may be formed in alternate shapes, e.g., spiral, and applied to the various embodiments of the present invention as a combustion system.

In addition to alternate combustion and vaporization features, alternative methods of hydrogen purification may be employed in a steam reformer under the present invention. In addition to tubular and concentric-tubular architectures, planar membrane structures may also be employed in a steam reformer with internal hydrogen purification.

A further embodiment of a steam reformer with internal hydrogen purification according to the present invention includes planar membrane structures. A third alternate reformer includes an outer metal tube having shoulders at each open end thereof. Within the outer tube, a metal reforming catalyst tube and a metal polishing catalyst tube lie in generally parallel relation along the length of the outer tube. As may be appreciated, however, a variety of geometric configurations and relationships between the metal reforming and metal polishing catalyst tubes may be employed. The reforming catalyst tube contains a reforming catalyst and establishes a reformation region. Similarly, the polishing catalyst tube contains a polishing catalyst and establishes a polishing region. An end plate and a gasket couple to a shoulder of the outer tube and seal the outer tube. An inlet port carries a liquid feed stock, e.g., methanol and water, through an end plate and into a vaporization coil. In the particular embodiment, the coil wraps about one end of the reforming catalyst tube and sits near the combustion exhaust port provided in the end plate. The vaporization coil couples to an end of the reforming catalyst tube whereby vaporized feed stock exits the coil and enters the reformation region.

A plate membrane module couples to a shoulder of the outer metal tube and seals an end of the outer metal tube to complete a combustion region within the outer tube, but external of the catalyst tubes. The plate membrane module couples to the reforming catalyst tube to receive a reformate-rich gas flow, couples to a first conduit to provide a product or hydrogen stream, and couples to a second conduit to provide a byproduct stream as fuel stock to support combustion in the combustion region. More than one reforming catalyst tube may be used. The byproduct stream, as in earlier-described embodiments of the present invention, intentionally includes a given amount of hydrogen not taken from the reformation process and applied to the combustion process. The second conduit carries the byproduct stream from the plate membrane module through a pressure let down valve and into the combustion region at the inlet port thereof. Adjacent the fuel inlet port, an air inlet port admits air, e.g., forced by blower, into the combustion region. Alternatively, a manifold, as in earlier-described embodiments of the present invention, may be used to admit air and the byproduct stream into the combustion region. As the byproduct stream enters the combustion region, and intermixes with the combustion air at the air inlet port, it continues past an igniter. The igniter initiates combustion of the mixture of the byproduct stream and combustion air thereby supporting a combustion process within the combustion region. As may be appreciated, heat developed in this combustion process supports vaporization of feed stock in the vaporization coil and thereby provides vaporized gasses to the reformation region. Heat from combustion in the combustion region also serves to directly heat the reforming region and to heat the polishing region.

The first conduit carries the product (hydrogen) stream into an end of the polishing catalyst tube. More than one such conduit and more than one polishing catalyst tube may be used. The product stream passes through the polishing region, where undesirable elements are neutralized, and the final purified hydrogen product passes from the other end of the polishing catalyst tube and out the outlet port. For example, when the polishing catalyst is a methanation catalyst, carbon monoxide and carbon dioxide present in the product stream are converted to methane as described previously.

The plate membrane module includes first and second end plates. A series of membrane envelope plates stack between the end plates. For example, three such membrane envelope plates may be stacked between the end plates. The end plates and membrane envelope plates are all generally rectangular and have corresponding dimensions. Other geometries, such as circular, may be used rather than a rectangular geometry. In other words, the end plates and membrane envelope plates stack like a deck of cards and couple together, e.g. by brazing, to form the plate membrane module. The second end plate is a solid planar structure. The first end plate, however, includes inlet and outlet ports for coupling to other portions of the third alternate reformer. In particular, the reformation catalyst tube couples to a reformate-rich inlet port to receive the products of reformation, i.e., to receive the reformate rich flow. The second conduit couples to a reformate-depleted outlet port to take from the plate membrane module the byproduct stream. The plate membrane module has first and second product outlet ports, providing the product stream. However, only one product outlet port may be used in some embodiments. The first conduit couples to the product outlet ports to collect the product stream therefrom. All of the inlet and outlet ports need not be located on the first end plate. Rather,

one or more of the ports may be located on the second end plate as desired or necessary in a particular configuration.

Each membrane envelope plate includes ports positioned in locations corresponding to the inlet and outlet ports of the first end plate. When stacked and operating as the plate membrane module, these various ports align and provide conduits to and from the filtration process executed by the module. Each of the membrane envelope plates includes a product port. The second product outlet port and the product ports align and cooperate to provide a conduit for the product stream out of the module and into the first conduit. As will be explained more fully hereafter, the product, i.e., hydrogen, enters the product ports laterally within the corresponding membrane envelope plate. Each of the membrane envelope plates includes also a port aligned with the first product outlet port of the first end plate. These ports also carry the product stream away from the plate membrane envelopes and into the first conduit. As with the product ports, these latter ports receive the hydrogen stream laterally from within the corresponding membrane envelope plate.

Three further ports align with the reformate-rich inlet port of the end plate and thereby provide a conduit for introduction of the hydrogen-rich reformate flow from the reforming catalyst tube and into the membrane envelope plates. Each of the plates includes a byproduct port. The byproduct ports align with the reformate-depleted outlet port of the first end plate to provide a conduit for the byproduct stream away from the membrane envelope plates. Forcing the hydrogen-rich reformate flow into the reformate-rich inlet port produces the byproduct flow at the reformate-depleted outlet port for application to the combustion process within the combustion region and produces the product stream for application to the polishing region.

Each of the membrane envelope plates itself includes a stack of individual plate elements. Each of the plate elements includes ports establishing communication through the membrane envelope as described above. Some of these ports, however, are "open" laterally into the corresponding plate element and thereby provide lateral access to portions of the module.

Each membrane envelope plate includes a left spacer plate and right spacer plate as the outer most plates in the stack. Generally, each of spacer plates are "frame" structures defining an inner open region. Each inner open region couples laterally to the inlet and outlet ports. The inlet port thereby admits the reformate-rich gas flow into the open region and the outlet port thereby carries the byproduct stream out of the open region. The product ports, however, are closed relative to the open region thereby isolating the product stream.

Each membrane envelope plate also includes a left membrane plate and a right membrane plate, each adjacent and interior to a corresponding one of the left and right spacer plates. These membrane plates each include as a central portion thereof a palladium alloy membrane secured to an outer metal frame. In these membrane plates, all of the ports are closed relative to the palladium alloy membrane. Each palladium alloy membrane lies adjacent to a corresponding one of the open regions, i.e., adjacent to the hydrogen-rich reformate flow arriving by way of the inlet port. This provides opportunity for hydrogen to pass through the palladium alloy membrane of the adjacent membrane plate. The remaining gasses, i.e., the byproduct stream, leave the open region through the outlet port.

A screen plate lies intermediate the membrane plates, i.e., on the interior or permeate side of each of membranes. The screen plate includes an outer frame and carries in a central region thereof a screen. The inlet and outlet

ports are closed relative to the central region of the screen plate, thereby isolating the byproduct stream and the reformate-rich flow from the product stream. The product ports are open to the interior region of the screen plate carrying the screen. Hydrogen, having passed through the adjoining membranes, travels along and through the screen to the product ports and eventually to the first conduit as the product stream.

As the hydrogen-rich reformate flow enters the reformate-rich inlet port and forces its flow against the membranes, hydrogen passes therethrough as the product stream and along the product ports. The byproduct stream diverts at the membranes and travels along the outlet port to the second conduit.

A variety of methods, including brazing, gasketing, and welding, may be used, individually or in combination, to achieve gas-tight seals between the spacer plates, the membrane plates and the screen plate, as well as between the membrane envelopes.

The screen not only provides a flow path for the product flow, but also bears the pressure differential applied to the membranes to force hydrogen, i.e., the product stream, across the membranes. It will be understood that a variety of structures may be used within an open region of the screen plate to provide the support function against pressure applied to the membranes and to provide a flow path for the product stream. To the extent that the palladium alloy membranes are better supported by an appropriate structure, e.g., the screen, thinner and less expensive palladium alloy membranes may be employed. Alternative materials to the screen include porous ceramics, porous carbon, porous metal, ceramic foam, carbon foam, and metal foam.

As discussed throughout this specification, use of thin, less expensive palladium alloy membranes significantly reduces the cost of a steam

reformer under the present invention. While it is recognized that use of such thin palladium alloy membranes will result in some contaminants passing into the product stream, subsequent purification steps may be taken, e.g., such as illustrated in several embodiments of the present invention.

Manufacturing steps taken in manipulation of the thin palladium alloy membranes, particularly in establishing a gas-tight seal relative to such membranes, must take into account the delicate nature of such thin palladium alloy membranes. In particular, conventional welding or brazing manufacturing steps, i.e., steps including a liquid-phase, cannot by applied to extremely thin (typically <50 microns) palladium alloy membranes. In particular, when liquid phase material contacts the thin palladium alloy membrane it dissolves and melts the membrane and, due to the extremely thin nature of the membrane, cannot serve as an acceptable manufacturing step. There are a variety of ways to establish a gas-tight seal relative to a thin palladium alloy membrane, however, the subject matter of the present invention proposes a particular method of manufacturing to achieve a gas tight seal of a thin palladium alloy membrane without causing significant damage to, i.e., leaks in, the palladium alloy membrane.

Under the present invention, a palladium alloy membrane may be attached and form a gas tight seal relative to an adjoining structure by means of an intermediate foil attached by ultrasonic welding. The method of manufacture proposed herein may be applied to the tubular form of membrane modules, e.g., such as shown in Fig. 3, or to plate form membrane structures described previously. Membrane tube 54 may then be coupled by brazing the foil to the end caps that seal the membrane tube. In the plate membrane form of the present invention, palladium alloy membranes carrying a foil may be attached by brazing

the foil to the surrounding frame of the left and right membrane plates. When applied to joining metals, ultrasonic welding strips away and cleans the metal surfaces to such extent that contact between such ultra-clean metals results in joining by solid state intermetallic diffusion. The ultrasonic action scrubbing the mating surfaces of the materials may be done under pressure such as 20 to 60 psi. Once these materials contact, the metal atoms diffuse together and thereby establish a gas tight seal. Important to note, ultrasonic welding does not require a liquid phase and when properly executed does not present opportunity for deterioration of a thin palladium alloy membrane. Because of the relatively low temperature requirements of ultrasonic welding, very little warping of material occurs. Accordingly, ultrasonic welding is particularly well suited for establishing a gas tight seal relative to an ultra thin palladium alloy membrane.

Ultrasonic welding may be used to attach a copper or nickel alloy foil to the surface of the thin palladium alloy membrane. Once this additional copper or nickel alloy layer has been attached it is brazed or welded to an adjoining material, e.g., the end caps or the surrounding outer metal frames.

The components and manufacturing steps used in constructing a membrane module, e.g., such as illustrated in Fig. 1 and otherwise described herein as a tubular palladium alloy structure supported with end caps, are described herein. Examples include a palladium alloy foil and a copper or nickel frame joined, respectively, in preparation for joining by ultrasonic welding, and the combined palladium alloy foil and copper or nickel frame assembly rolled into a tubular structure and again joined by ultrasonic welding to maintain the tubular structure. In this configuration, the end portion of the tubular assembly bears exposed sections of copper or nickel material. The end caps are then

brazed directly to this exposed portion of copper or nickel frame to complete the gas-tight structure.

For example, a tubular hydrogen-permeable metal membrane was prepared by the following general method of construction. Both Pd-40Cu and Pd-25Ag foil (nominally 25 micron thick) were used as the hydrogen-permeable membrane. A tension spring, composed of either carbon steel or stainless steel, was used as support within the tubular membrane structure.

The first step was to join the palladium-alloy foil to the copper foil frame (nominally 50 microns to 125 microns thick). The palladium-alloy foil was typically 8.9 cm wide by 26.4 cm long, and the copper foil frame was typically 10.2 cm wide by 27.9 cm long with a cut out center, equally spaced from all four sides, approximately 7.6 cm wide by 24.1 cm long. This provided a 0.6 cm overlap between the palladium-alloy foil and the copper foil frame as the foil occupied the cut out center of the copper foil frame.

Ultrasonic welding was used to establish peripheral gas-tight seals between the palladium-alloy foil and the copper foil frame at all four edges of the palladium-alloy foil. An Amtech (Shelton, CT) ULTRASEAM™ Model 40 welder was used. This welder operates at 40 kHz and delivers up to about 750W of power to the ultrasonic transducer. Both the horn (connected to the ultrasonic transducer) and the anvil rotate at a rate selected by the operator during normal operation of the welder. Welding is accomplished by placing metal between the horn and anvil and applying power to the ultrasonic transducer.

The horn and anvil for the ultrasonic welder are circular, 7.0 cm diameter, with a bearing surface strip about 0.2 cm wide and finished to a surface roughness equivalent to an EDM #3 finish. The horn and anvil were hard coated with titanium nitride. Typical welding parameters are: 40% full power to the

transducer, 40 psig applied pressure between the horn and the anvil, 4 rpm rotation rate for the horn and anvil, and the horn "floating" on the foil pieces to be welded (i.e., no preset separation between the horn and anvil). To ensure that the metals are bonded during the welding process, the adjoining metal surfaces should be cleaned of residues such as oxidation, grease and oils, dirt, etc. It is also considered beneficial if the palladium-alloy membrane foil and the copper foil frame are annealed prior to welding, since soft metals are more reliably joined by ultrasonic welding than are hard metals.

After welding the palladium-alloy foil to the copper foil frame to establish the membrane assembly, the welded seals were examined for leaks by a standard dye penetration test. If no leaks were found, the membrane assembly was cleaned of excess dye and then wrapped, lengthwise around a 2.8 cm (outside diameter) tension spring, 27.9 cm long and made from either stainless steel or carbon steel wire nominally 0.25 cm diameter. The overlap of opposite edges of the membrane assembly was then joined by ultrasonic welding to form a lap seal along the length of the now tubular structure. The lap seal was established by using the ultrasonic welding parameters specified above. The lap seal was then folded over against the membrane tube to conform to a cylindrical shape. Copper end caps were then fitted to the membrane tube ends and brazed in place at braze joints using standard copper/phosphorous or copper/silver/phosphorous brazing alloys and a hydrogen/air or hydrocarbon/air (e.g., methane, propane, or acetylene) torch. The brazing alloy is applied only to the copper end caps and the copper foil frame. Important to note, establishing the braze joints coupling the end caps to the cylindrical form of the membrane assembly does not expose the delicate palladium alloy membrane foil to liquid phase material, i.e., does not destroy the delicate, thin foil. Because the various

ultrasonic welds establish a gas-tight seal and the braze joints also establish a gas-tight seal, hydrogen passes from a reformation process external of the metal membrane tube only through the membrane foil. At least one end cap was fitted with a port and an outlet to collect the permeate hydrogen from the inside, or bore, of the membrane tube. Within the metal membrane tube, a methanation catalyst may be employed whereby purified hydrogen may be taken from the membrane tube as described herein-above. Thus, membranes so constructed are suitable for the high pressure feed gas to be passed over the external surface of the membrane tube, with the permeate collected at the interior surface of the membrane.

A steam reformer according to another embodiment of the present invention employs an isolated vaporization chamber similar to that of the third alternate reformer. More particularly, a fourth alternate reformer receives at an input conduit a feed stock and the conduit delivers this mixture into the isolated vaporization chamber at the vaporization coil. Elevated temperatures within the vaporization chamber vaporize the feed stock provided at the input conduit. The vaporization coil passes into and opens into a reformation chamber. Vaporized fuel thereby enters the reformation chamber. The chamber is filled with a reformation catalyst and steam reformation occurs within the steam reformation region. A reformation product stream exits the reformation region at the outlet conduit. The outlet conduit delivers the product stream to a membrane module. The module separates the product stream into a byproduct stream and a hydrogen-rich stream.

The hydrogen-depleted reformate byproduct stream travels along a conduit from the membrane module to a pressure let down valve and then to a manifold. The manifold operates in similar fashion to the manifold of the first

alternate reformer. More particularly, the manifold introduces an air supply taken from an inlet, e.g., from a forced air supply, and intermixes it with the byproduct stream at a mixing region. An igniter ignites the intermixed air and byproduct stream and the resulting combustion elevates temperatures within the vaporization chamber. As in earlier described embodiments of the present invention, the byproduct stream includes by design a certain amount of hydrogen not taken across the palladium alloy membranes of the membrane module. The byproduct stream thereby serves as a fuel source for combustion within the vaporization chamber.

Exhaust ports carry the combustion byproducts from the vaporization chamber through combustion conduits and out exhaust ports. The combustion conduits, however, pass through the reformation chamber and thereby distribute heat throughout the reformation region in support of the reformation process therein. The combustion conduits may take a variety of forms, including finned tubes and spirals, to provide substantial surface area and desirable uniform distribution of heat throughout the reformation region.

The product stream emerging from the membrane module travels through a conduit having therein a methanation catalyst. This conduit passes through the reformation region and through the vaporization chamber and thereby collects heat energy therefrom in support of the methanation process occurring in the conduit. The distal end of the conduit provides a product outlet, i.e., provides hydrogen in sufficiently purified form for application to, for example, PEM fuel cell 16 (Fig. 1).

The membrane frame employed in the membrane module includes a circular copper or nickel frame with a rectangular center cut out. A rectangular palladium alloy membrane, oversized relative to the center cut out, is joined at

seals to the frame. By using ultrasonic welding to establish the seals about the periphery of the rectangular palladium alloy membrane, a gas-tight seal results between the membrane and the frame. Finally, the membrane frame includes a feed manifold aperture and a permeate manifold aperture.

The permeate frame of the membrane module includes a central cut out. The cut out includes a first portion generally rectangular and corresponding generally in dimension to the rectangular membrane. This portion of the cut out is occupied by a wire mesh spacer. Other materials that may be used in place of the wire mesh spacer include porous and foamed ceramic, porous and foamed carbon, and porous and foamed metal. A second portion of the cut out extends peripherally outward to define a permeate manifold and containing therein a wire mesh insert. The permeate frame may be recessed to accommodate face-to-face contact with the membrane frame, i.e., to accommodate the rectangular membrane as attached to the face of the membrane frame. Finally, the permeate frame includes a feed manifold aperture.

As may be appreciated, the membrane frame and the permeate frame correspond in outer dimensions and certain portions align when stacked. For example, the feed manifold aperture of the membrane frame aligns with the feed manifold aperture of the permeate frame. Also, the permeate manifold aperture of the membrane frame may be aligned with the substantially larger permeate manifold of the permeate frame. Thus, when appropriately stacked with other components, described more fully hereafter, a membrane module may be established to separate the reformation product stream into the hydrogen-rich and byproduct streams as described herein-above.

The membrane and permeate frames may be stacked to form a series flow arrangement for the membrane module. The permeate frame

occupies a central position with a membrane frame on each side, i.e., above and below. The feed manifold aperture of the permeate frame aligns with the feed manifold apertures of the membrane frames. The permeate manifold of the permeate frame aligns with permeate manifold apertures of the membrane frames. Feed frames are located at the outward side of each of the membrane frames, i.e., above and below the membrane frames. Each feed frame is of circular shape corresponding to that of the membrane and permeate frames. Each feed frame includes an open central region extending laterally outward to correspond with, i.e., to fluidly couple with, aligned feed manifold apertures of the membrane and permeate frames. Each feed frame also includes a permeate manifold aperture isolated relative to the center cut out portion.

Thus, this arrangement offers a series flow configuration directing the feed gas sequentially across successive palladium alloy membranes. For example, consider a feed gas traveling upward through the component stack. As the feed gas enters the center open region of the lowest feed frame, hydrogen has opportunity to pass through the membrane of the lowest membrane frame. As may be appreciated, any such hydrogen which does cross the lowest membrane frame migrates into the open region of the permeate frame and can then migrate by way of the permeate manifolds of the permeate, membrane and feed frames, out of the component stack for harvest. The series flow arrangement offers a second opportunity for feed gas to pass through a membrane. More particularly, feed gas travels from the open center region of the lowest feed frame into the feed manifold of the lowest membrane frame, through the feed manifold of the permeate frame, through the feed manifold of the upper membrane frame, and into the central open region of the upper most feed frame. In this open central region, the feed gas is exposed to a second palladium alloy membrane. More

particularly, hydrogen remaining in the feed gas as it enters the open region of the upper feed frame is exposed to the membrane of the upper membrane frame. Any such hydrogen crossing this upper membrane enters the central open region of the permeate frame and may then travel along the permeate manifolds for harvest.

As may be appreciated, additional similar components may be stacked in this arrangement to provide successive opportunity for feed gas exposure to palladium alloy membranes in series fashion. An actual implementation would include end plates and necessary outlet and inlet ports for harvesting hydrogen gas and forcing feed gas into the component stack as described earlier in connection with the plate form membrane module described above in connection with the third alternate reformer.

In such series flow arrangement, the feed gas stream is directed to flow over a first membrane surface, then a second membrane surface, and so on as desired. Such series flow arrangement encourages mixing of the feed gas stream components after passage over each membrane in the membrane module component stack.

A further alternative arrangement for membrane module components is to provide a parallel flow configuration, i.e., where the feed stock stream divides and has one opportunity for exposure to a palladium alloy membrane. In this arrangement, membrane frames correspond generally to the previously described membrane frames, but include also a raffinate manifold. Similarly, a permeate frame corresponds to the previously described permeate frame, but includes also a raffinate manifold. The raffinate manifolds align for fluid communication therebetween when the membrane and permeate frames stack.

This arrangement establishes a parallel flow of feed gas across the palladium alloy membranes. More particularly, consider a feed gas entering the open central region of the lower feed frame. Such feed gas is exposed to the membrane of the lower membrane frame. Concurrently, some of the feed gas may divert across the lower membrane and then travel along the raffinate channels established by the raffinate manifolds, or along the feed manifolds of the membrane and permeate frames and eventually enter the open region of the upper feed frame. At this point, the feed gas is exposed to the membrane of the upper membrane frame. Accordingly, hydrogen present therein may migrate across the membrane and into the center open region of the permeate frame. Thereafter, such hydrogen would pass along the permeate manifolds of the permeate and membrane frames and eventually through the permeate manifold apertures of the feed frame for harvest. In such parallel flow configuration, all of the feed channels over the membrane surfaces are fed from a common feed supply manifold. This favors low pressure drop for the flowing feed gas stream.

The arrangement of membrane component stacking allows series or parallel, respectively, flow of the feed gas through the membrane module. Because the feed frames are compatible, it is possible to combine series flow and parallel flow stacking arrangements in a single membrane module. More particularly, an arrangement may be stacked adjacent to an arrangement. Multiple combinations of such arrangements may be provided in a single membrane module as desired to establish a given first-stage of the hydrogen purifier.

An additional frame component which may be incorporated into a membrane module is an exhaust frame, which includes a feed manifold aperture, a permeate manifold, and a raffinate manifold. As may be appreciated, stacking

the exhaust frame in a membrane module allows passage of feed gas through the feed manifold aperture, hydrogen product through the permeate manifold, and passage of raffinate through the raffinate manifold without otherwise affecting operation of the membrane modules as described herein above. The exhaust frame includes also an exhaust manifold providing a lateral passage for hot combustion exhaust gas through the exhaust frame. As may be appreciated, the exhaust manifold is isolated relative to the feed manifold aperture and the permeate and raffinate manifolds. Hot exhaust gas passing through the exhaust frame elevates the temperature of a membrane module including the exhaust frame and thereby speeds heating of the membrane module during start up. The exhaust frame may be incorporated into the stacked component structure of a membrane module along with the other frame members by conventional brazing, gasketing, or welding techniques as described herein.

Stacking and construction of the planar-type components may be executed by use of conventional brazing, gasketing, or welding methods to create a stacked component membrane module. To establish seals between the stacked components of the modules, i.e., the membrane assemblies, permeate and feed frames, exhaust frame members, and end plates, brazing, gasketing, or welding methods are appropriate and may be used without deterioration of the delicate palladium alloy membranes. For example, brazing alloy may be applied between adjoining frame elements and the entire assembly heated to achieve a brazed joint within a controlled-atmosphere brazing furnace. Alternatively, the module may be assembled then welded from the exterior, for example, by using an orbital pipe-welding machine. In yet another proposed method of manufacture of a sealed membrane module, the components are stacked and sufficient pressure applied to the stack such that all joining surfaces are in intimate

pressurized contact. Then, heating the entire assembly to between 500 and 800 degrees Celsius for two hours to eight hours results in intermetallic diffusion between the adjoining surfaces to create a sealed joint. Yet another method for achieving gas-tight seals is to use conventional flexible (compressible) graphite gaskets or composite graphite-metal gaskets.

Thus, a variety of embodiments, configurations and alternatives have been shown for implementing steam reformation under the present invention. Various experiments and testing procedures have been conducted to prove the viability of steam reformation under the present invention and will be described in general terms as follows.

As disclosed earlier in the preferred embodiments of the present invention, the hydrogen-rich reformate stream is purified by means of a two-stage hydrogen purifier that is also the subject of this invention. The two-stage hydrogen purifier utilizes a membrane for the first stage to accomplish a bulk separation of hydrogen from the reformate stream. Then, the permeate hydrogen from the first-stage membrane is subjected to a polishing step (the second stage) to further reduce the concentration of selected impurities, such as CO and CO_2, to acceptably low levels as required for the hydrogen to serve as the fuel for PEM fuel cells. For instance, a typical PEM fuel cell using a standard platinum electrocatalyst requires hydrogen containing <10 ppm CO and, preferably, <100 ppm CO_2 to achieve maximum power output from the fuel cell.

The membrane used in the first stage of the purifier is selected from hydrogen-permeable and hydrogen-selective high-temperature membranes. Thermally-stable membranes allow the purifier to be thermally integrated with the reformer, eliminating the requirement for cooling the hydrogen-rich reformate prior to purification, thereby simplifying the overall system and reducing the cost of the system.

Preferred membranes are microporous ceramic, microporous carbon, microporous metallic, and dense metallic membranes. Especially preferred are thin membranes composed of hydrogen-permeable and hydrogen-selective metals including palladium and palladium alloys, nickel and nickel alloys, and the Group 4 and Group 5 metals and their alloys. Thin membranes composed of Pd-40Cu are especially preferred for high hydrogen permeability and durability. In particular, the Pd-40Cu alloy exhibits highest hydrogen permeability and, therefore, most favorable economics,

if the Pd-40Cu alloy contains low concentrations of carbon and oxygen. The following table demonstrates the correlation between high hydrogen permeability (represented as hydrogen flux through the 25 micron thick membrane at 100 psig hydrogen, 400 degrees Celsius) and low carbon content.

Hydrogen Flux	Concentration, ppm		
std. $ft^3/ft^2 \bullet hr$	Carbon	Oxygen	Silicon
130	40	25	10
125	56	29	39
115	146	25	15
56	219	25	27

The hydrogen-permeable membrane does not have to exhibit an exceptionally high selectivity for hydrogen over other gases, since the second stage of the hydrogen purifier serves to further reduce the concentration of selected impurities that remain in the permeate hydrogen after passing through the membrane. Selectivity is defined as the ratio of the permeation rate of hydrogen divided by the permeation rate of an impurity. The selectivity for hydrogen exhibited by the membrane is at least 20, and preferably at least 50.

Use of such membranes with relatively low selectivity will not yield a permeate hydrogen stream that is of acceptable purity for use in a PEM fuel cell. For example, steam reforming methanol yields a hydrogen-rich reformate stream containing about 25% combined CO and CO_2. A membrane with a hydrogen selectivity of 50 will produce a permeate hydrogen stream containing 25%/50 = 0.5% combined CO and CO_2. However, this level of impurities is readily treated with the polishing step (the second stage). Thus, the two-stage hydrogen purifier allows the use of membranes

that, due to imperfections or otherwise, have relatively low selectivity for hydrogen over other gases. Such membranes are much less expensive than are membranes that have substantially higher hydrogen selectivity (e.g., hydrogen selectivity >1000).

To obtain a very thin metal hydrogen-permeable membrane without sacrificing mechanical strength of the membrane, the thin hydrogen-permeable membrane is supported by a support layer. The support layer must be thermally and chemically stable under the operating condition of the membrane, and the support layer is preferably porous or containing sufficient voids to allow hydrogen that permeates the thin membrane to pass substantially unimpeded through the support layer. Examples of support layer materials include metal, carbon, and ceramic foam, porous and microporous ceramics, porous and microporous metals, metal mesh, perforated metal, and slotted metal. Especially preferred support layers are woven metal mesh (also known as screen) and tubular metal tension springs.

In the event that the membrane is a thin hydrogen-permeable metal (e.g., palladium alloys) and the support layer is composed of a metal, the metal used for the support layer is preferably selected from a corrosion-resistant alloy, such as stainless steels and non-ferrous corrosion-resistant alloys comprised of one or more of the following metals: chromium, nickel, titanium, niobium, vanadium, zirconium, tantalum, molybdenum, tungsten, silicon, and aluminum. These corrosion-resistant alloys have a native surface oxide layer that is chemically and physically very stable and serves to significantly retard the rate of intermetallic diffusion between the thin metal membrane and the metal support layer. Such intermetallic diffusion, if it were to occur, often results in significant degradation of the hydrogen permeability of the

membrane and is undesirable [see Edlund, D.J., and J. McCarthy, "The Relationship Between Intermetallic Diffusion and Flux Decline in Composite-Metal Membranes: Implications for Achieving Long Membrane Lifetimes" *J. Membrane., 107* (1995)147-153].

The rate of intermetallic diffusion between the thin metal membrane and the metal support layer may also be retarded by applying certain non-porous coatings to the metal support. Suitable coating materials include aluminum oxide; aluminum nitride; silicon oxide; tungsten carbide; tungsten nitride; oxides, nitrides, and carbides of the Group 4 and Group 5 metals; boron nitride; and boron carbide. Many of these coating are employed as hard coatings on tools and dies, and as release agents.

The second stage of the hydrogen purifier is designed to further reduce the concentration of impurities that adversely affect the power output and operation of the PEM fuel cell. Particularly, the second-stage polishing step is designed to remove CO and, to a lesser degree, CO_2 from the hydrogen that has permeated the first-stage membrane. Furthermore, the second-stage polishing step is conducted at or near the operating temperature of the first-stage membrane and the reformer, thereby eliminating the need to substantially heat or cool the hydrogen stream before passage through the polishing step. By thermally integrating the polishing step, the need for heat exchangers is eliminated and the overall operation of the system is simplified and the cost of the system is reduced.

Suitable chemical operations for the second-stage polishing step include preferential oxidation of CO, a widely practiced method for removing CO from hydrogen fuel streams for PEM fuel cells [Swathirajan, S., and H. Fronk, "Proton-

Exchange-Membrane Fuel Cell for Transportation" *Proceedings of the Fuel Cells '94 Contractors Review Meeting*, DOE/METC-94/1010, August 17-19(1994)105-108]. However, selective oxidation only removes CO from the hydrogen stream, it does not reduce the CO_2 content. In fact, selective oxidation increases the CO_2 content of the hydrogen. A preferred chemical operation for the polishing step is methanation, which removes both CO and CO_2 from the hydrogen stream, as represented by the following chemical reactions:

$$CO + 3\,H_2 = CH_4 + H_2O$$

$$CO_2 + 4\,H_2 = CH_4 + 2H_2O$$

Methanation occurs rapidly at >300°C in the presence of a catalyst, such as nickel, palladium, ruthenium, rhodium, and platinum. Preferably, methanation is conducted at 400°C to 600°C in the presence of a commercial supported nickel reforming or methanation catalyst such as R1-10 and G1-80 manufactured and sold by BASF.

As the embodiments described earlier have shown, the first stage and second stage of the hydrogen purifier can be integrated so that they are in close proximity, thereby minimizing heat loss as well as reducing the size, weight, and cost of the hydrogen purifier. For example, if a tubular membrane is used as the first stage, the second-stage polishing step may be located within the bore of the membrane tube at the permeate side of the membrane. If a plate-type membrane is selected, the polishing step may be located at the permeate side of the membrane between membrane plates, or it may be located in a tube or other shape that is directly connected to the plate-type membrane at the permeate-hydrogen discharge port. Furthermore, if the membrane is supported for strength, and if the polishing step is

methanation, the methanation catalyst may be incorporated within the support for the membrane. For instance, the membrane support may comprise a nickel or other metal mesh with a high nickel surface area.

While previously disclosed embodiments of the invention have shown the two-stage hydrogen purifier as an integral part of the fuel processor, it will be appreciated that the two-stage hydrogen purifier may function external to a conventional process for hydrogen manufacture (e.g., steam reformer, partial-oxidation reactor, or autothermal reformer).

Concerns over safety call for use of non-flammable fuel feedstocks for use to produce hydrogen by the steam-reforming process. The advantages of using non-flammable fuel feedstocks include elimination of fire or explosion danger due to vapors from the fuel feedstock accumulating in enclosed environments and, for military applications, elimination of fire or explosion risk from hot metal fragments striking and penetrating fuel storage tanks.

Non-flammable fuel feedstocks for generating hydrogen by steam reforming and as disclosed in this invention include polyhydroxy alcohols and polyethers that are miscible with water. As used herein, non-flammable means that combustion in normal air at about 1 atm. pressure is not self-sustaining. Preferred fuels include ethylene glycol, propylene glycol, and the glycol ethers of ethylene glycol and propylene glycol (e.g., diethylene glycol). These fuels are collectively called glycols. When mixed with a stoichiometric amount of water for steam reforming (e.g., two molar equivalents water to one molar equivalent ethylene glycol; and four molar equivalents water to one molar equivalent propylene glycol), these fuel feedstocks are

not flammable even when subjected to a propane/air flame from a torch. The flame merely heats the glycol/water mixture until the water in the mixture boils. Provided substantial water is still present in the glycol/water mixture, combustion is not supported.

The non-flammable nature of the glycol/water mixtures is due to the very low vapor pressure of the glycol component (e.g., ethylene glycol and propylene glycol). For instance, the vapor pressure of ethylene glycol is only 20 torr at 100°C. Furthermore, the water component of these mixtures, in addition to being a necessary reactant for steam reforming, serves two functions that contribute to the non-flammable nature of these glycol/water mixtures. First, water in the mixture serves, by evaporative cooling, to reduce the maximum temperature to which the mixture can be heated thereby limiting the maximum vapor pressure of the glycol. Second, as water evaporates at the surface of the mixture, the water vapor dilutes oxygen (from air) at the surface of the glycol/water mixture. Since oxygen is necessary for combustion, and combustion is generally favored by high oxygen concentrations, substantial dilution of oxygen from air by evaporating water serves to reduce the flammability of the glycol/water mixture.

Thus, certain feedstock mixtures are non-flammable. Simply stated, to be non-flammable the vapor pressure of the combustible component, i.e., organic component, of the fuel feedstock must remain below the lower flammability limit at 100°C; the approximate temperature at which water in the mixture will boil. Generally, this requires that the organic component have a vapor pressure <100 torr at 100°C.

In addition to being non-flammable, glycol/water mixtures, best known for their use as heat exchange fluids in internal combustion engines, are converted to a hydrogen-rich reformate stream in the presence of nickel-based steam-reforming catalysts at temperatures in the range of 400°C to 700°C. Glycol/water mixtures also offer the advantage of forming stable solutions over a wide range of water concentration, so that the proper water to glycol steam reforming ratio can be obtained by appropriately mixing the glycol/water fuel feedstock and then dispensing this fuel feedstock into a supply tank (or reservoir) from which the fuel feedstock is delivered at the proper rate to the reformer. Yet another advantage of the glycol/water mixtures is that they remain liquid over a large temperature range, and they are generally viscous liquids. Glycol/water mixtures, sold commercially as antifreeze coolants, remain liquid even at temperatures well below 0°C and at temperatures greater than 100°C. Being liquid, glycol/water mixtures are efficiently pumped to elevated pressure for delivery to the reformer so that steam reforming can be conducted at elevated pressure (up to 500 psig, but preferably 100 psig to 300 psig). The high viscosity of glycol/water mixtures leads to greater pumping efficiency, particularly if a gear pump, piston pump, or centrifugal pump is used to deliver the high-pressure fuel feedstock to the reformer. The high viscosity reduces slippage past the wetted surfaces of the pump, which often limits the maximum pressure differential at which a pump may be used.

To demonstrate the integrated fuel processor of this invention, a fuel processor, such as the first alternate reformer described above, was constructed and operated. The tubular metal membrane (first stage of the hydrogen purifier) was made using the method generally described herein. The hydrogen-permeable metal foil consisted of Pd-40Cu nominally 25 microns thick, and the membrane was about 15 cm long (2.8 cm outside diameter). The second stage of the hydrogen purifier, a catalytic methanizer, was contained in a copper tube, 1.8 cm outside diameter, that was inserted inside the bore of the tubular membrane. One end of the copper methanation tube was sealed to one of the tubular-membrane end caps. The other end of the copper methanation tube was terminated about 0.3 cm from the end of the membrane tube whereby hydrogen permeating to the inside of the membrane tube would freely flow into the open end of the methanation tube such as shown generally in Figure 3. The

methanation tube was filled with catalyst G1-80 (BASF), a supported nickel composition that is active for methanation of CO and CO_2.

The reforming region of the fuel processor was filled with catalyst K3-110, a copper/zinc supported catalyst sold by BASF generally for conducting the water-gas shift reaction at <350°C. The shell of the fuel processor, the spiral combustion tube, and the end plates were all constructed from stainless steel. Insulation was placed around the exterior of the shell and end plates to reduce heat loss.

The fuel processor was operated using methanol/water mix as the feed. The methanol/water solution was prepared by mixing 405 mL methanol (histological grade, Fisher Scientific) with 180 mL deionized water. The fuel processor was heated to 200°C to 300°C using an externally placed electric resistance heater. Once the fuel processor was hot, the electric heaters were turned off and methanol/water solution was pumped into the fuel processor at 200 psig. The methanol/water feed was first vaporized then the vapors passed over the K3-110 reforming catalyst to produce

hydrogen-rich reformate. The two-stage hydrogen purifier then extracted product hydrogen at ambient pressure from the hydrogen-rich reformate. The hydrogen-depleted raffinate was directed to the combustor as described above. Combustion of this raffinate gas inside the fuel processor heated the fuel processor to 300°C. to 350°C and provided all required heat once operation of the fuel processor commenced.

The purity of the product hydrogen was determined by gas chromatography and the flow rate of the product hydrogen was measured using a calibrated gas flow meter. Analysis of the product hydrogen confirmed <10 ppm CO and <10 ppm CO_2. The flow rate of product hydrogen was 2 L/min. The reformer was operated in this mode, without any external source of heating, for 6 hours at which time the experiment was concluded.

According to a second example, tubular Pd-25Ag membranes with a 2.2 cm outside diameter were made using the general method described herein. The Pd-25Ag foil was 25 micron thick and 7.0 cm wide by 16 cm long and the copper foil frame was 125 micron thick and 8.3 cm wide by 17.8 cm long. The dimensions of the center cut out in the copper foil frame was 5.7 cm wide by 14 cm long. The welding equipment and methods described herein were used to join the palladium-alloy foil to the copper foil frame. The support for the membrane was a carbon steel tension spring, 2.2 cm outside diameter. The spring was made using wire nominally 0.25 cm diameter. End caps were brazed to the ends of the membrane tube using the method given above or, in some cases, end caps were sealed to the ends of the membrane tube using graphite seals. The graphite seals were achieved using flexible graphite tape (1.3

cm wide) wrapped around the membrane tube and then compressed against the membrane in a standard compression fitting.

In another example, plate-type membrane modules were made using the following general method. Hydrogen-permeable Pd-40Cu foil, nominally 25 micron thick and 5.1 cm by 5.1 cm square, were welded to a copper foil frame (nominally 125 micron thick) using the ultrasonic welder and welding parameters discussed above. The copper foil frame was circular in shape (8.9 cm diameter) with cut outs for feed and permeate. After welding the Pd-40Cu membrane to the copper foil frame to make the membrane assembly, the weld was checked for leaks by a standard dye penetration test.

The copper permeate plate was 0.3 cm thick and 8.9 cm diameter. A recessed was machined in the permeate plate to accept the support layer for the membrane. This recess was of the same dimensions as the membrane and connected to the permeate manifold channel. The support layer consisted of a first layer of stainless steel screen (70x70 mesh), placed against the permeate plate, then a second layer of stainless steel screen (200x200 mesh) that the thin Pd-40Cu foil rested against. This combination of coarse mesh and fine mesh was determined to both adequately support the thin membrane without excessively damaging the membrane, and provide acceptably low resistance to the lateral flow of permeate hydrogen.

The stainless steel screen was fixed to the permeate plate with a single drop of cyanoacrylate glue, and the glue allowed to dry. Then, two membrane assemblies were brazed to a single permeate plate, one membrane assembly at each major surface of the permeate plate. Brazing was achieved using a standard brazing

alloy (nominally 80% copper, 15% silver, and 5% phosphorous) in either ribbon form or as a paste (powdered brazing alloy mixed with a paste binder). This brazing alloy was purchased from Lucas-Milhaupt, Inc. (Cudahy, WI). To prevent unwanted creep of the brazing alloy over the surface of the Pd-40Cu membrane, NICROBRAZ™ Red Stop-Off Type II (Wall Colmonoy Corp., Madison Hts., MI) was applied around the edge of the Pd-40Cu membrane. This assembly was then placed on a flat surface beneath a steel weight (approximately 1.5 kg) and heated to 750°C in a brazing furnace. A coating of boron nitride, a release agent, was applied to the steel surfaces in contact with the membrane assembly during brazing to prevent sticking between the membrane assembly and the steel surfaces. Brazing was done under vacuum, a nitrogen atmosphere, or a nitrogen stream containing a low concentration of methanol or hydrogen to serve as a reducing gas (to prevent oxidation). The brazing temperature of 750°C was held for 15 minutes prior to cooling.

To demonstrate the non-flammability of ethylene glycol/water mixtures, the following experiment was conducted. Ethylene glycol (1.0 mL) was mixed with two molar equivalents water (0.65 mL). The resulting homogeneous solution is of the proper stoichiometry for steam reforming, as shown by the following ideal reaction equation:

$$\mathbf{HOCH_2CH_2OH + 2\,H_2O = 2\,CO_2 + 5\,H_2}$$

This solution of ethylene glycol and water was directly exposed to the flame from a propane/air torch. The ethylene glycol/water solution did not burn or support combustion.

In yet another example, a 2:1 molar ratio of water-to-ethylene glycol was prepared by mixing 65 mL deionized water and 100 mL purified reagent grade (Fisher Scientific) to form a homogeneous solution. This ethylene glycol/water solution was reformed to produce hydrogen in a laboratory-scale packed-bed catalytic reactor as described below.

The catalytic reactor consisted of a cylindrical stainless steel shell 2.5 cm inside diameter and 22.9 cm long. The reactor contained a fixed bed of the commercial catalyst G1-80 (BASF), which is a supported nickel steam reforming catalyst. A length of stainless steel tubing (0.3 cm diameter by about 25 cm long) was coiled around one end of the catalytic reactor to serve as a preheater and vaporizer for the ethylene glycol/water feed. One end of this vaporization coil was connected to the inlet of the catalytic reactor, the other end of the coil was connected to a reservoir containing the ethylene glycol/water feed. The temperature within the catalytic reactor was measured and controlled via a thermocouple inserted within the catalyst bed.

The catalytic reactor was heated to 500°C by means of an external electric furnace. The G1-80 catalyst was then reduced in situ by first flowing ethylene glycol/water feed into the catalytic reactor at a rate of 2.5 mL/min (liquid flow rate) for 2 hrs, then flowing pure hydrogen at ambient pressure through the catalytic reactor for another 4 hrs. Following reduction of the steam reforming catalyst, ethylene glycol/water feed was admitted into the catalytic reactor at ambient pressure. The temperature of the catalytic reactor was varied between 400°C and 500°C. The product gas was shown to be predominantly CO_2 and H_2 by gas chromatography analysis, unreacted ethylene glycol/water was collected in a cold trap and quantified by

gravimetric analysis, and the product flow rate was measured using a calibrated gas flow meter to determine the degree of conversion to products. The results of these experiments are summarized in the following table.

Temperature (°C)	Product Flow Rate (L/min)	Conversion to Products (%)
500 +/- 50	3-5	90-95
465 +/- 25	4-5	90-95
400 +/- 25	4-5	93-98

To demonstrate the utility of the two-stage hydrogen purifier when utilized as a stand-alone hydrogen purifier, the following experiment was conducted.

A tubular hydrogen-permeable metal membrane was made using the method herein. The membrane consisted of Pd-25Ag foil nominally 25 micron thick and was 2.2 cm outside diameter by 15 cm long, the overall length of the membrane tube (including end caps) was approximately 21 cm. This tubular membrane serves as the first stage of the purifier. The second stage of the purifier, a catalytic methanizer, was contained in a copper tube, 1.58 cm outside diameter, that was inserted inside the bore of the tubular membrane. One end of the copper methanation tube was sealed to one of the tubular-membrane end caps. The other end of the copper methanation tube was terminated about 0.3 cm from the end of the membrane tube so that hydrogen permeating to the inside of the membrane tube would freely flow into the open end of the methanation tube (this arrangement is shown in Figure 3). The methanation tube was filled with catalyst G1-80 (BASF), a supported nickel composition that is active for methanation of CO and CO_2.

This two-stage hydrogen purifier was placed in a stainless steel shell equipped with electric resistance heaters. The hydrogen purifier was heated to 300°C

to 350°C, and methanol/water reformate (approximately 70-75% hydrogen, balance CO and CO_2) at 50 psig was passed into the stainless steel shell and over the exterior surface of the Pd-25Ag membrane tube. Product hydrogen at ambient pressure, after permeation through the Pd-25Ag membrane and then passage over the methanation catalyst, was collected and analyzed by gas chromatography. Analysis confirmed that the product hydrogen contained <2 ppm CO and <50 ppm CO_2.

Thus, a steam reformer with internal hydrogen purification has been shown and described. The reformer of the present invention utilizes a single feed, e.g., a methanol and water or hydrocarbon and water mix, as both the chemical feed stock to support hydrogen reforming and also as a combustion fuel source to provide sufficient temperature to support steam reforming. The present invention recovers by design less than a maximum amount of hydrogen available in a reforming step to leave in the byproduct stream sufficient hydrogen as fuel to support the combustion process.

The present invention uses two distinct hydrogen purification processes. First, a membrane produces a hydrogen stream as a bulk filtration step, but the product hydrogen stream may still contain some undesirable impurities. Second, a polishing process converts the undesirable impurities in the hydrogen stream to innocuous components not affecting operation of, for example, a fuel cell. Advantageously, this allows use of a relatively less expensive, thin palladium-alloy membrane in the steam reforming process.

It will be appreciated that the present invention is not restricted to the particular embodiment that has been described and illustrated, and that variations may

be made therein without departing from the scope of the invention as found in the appended claims and equivalents thereof.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A steam reformer, comprising:

a shell having an outer surface and being adapted to receive a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol;

a reforming region within the shell and including a reforming catalyst bed adapted to receive the feedstock and convert the feedstock into a reforming product stream comprising hydrogen, carbon monoxide and carbon dioxide; and

a hydrogen purification module including a hydrogen-selective membrane in fluid communication with the reforming catalyst bed and adapted to produce a permeate stream comprised of a portion of the reforming product stream which passes through the membrane, and a byproduct stream comprised of a portion of the reforming product stream which does not pass through the membrane, wherein the hydrogen-selective membrane comprises palladium, copper and silicon, and further wherein the hydrogen-selective membrane contains 10–39 ppm silicon.

2. The reformer of claim 1, wherein the reformer further includes a polishing catalyst bed including a methanation catalyst, wherein the polishing catalyst bed is in fluid communication with the hydrogen purification module and is adapted to receive the permeate stream therefrom and reduce the concentration of carbon dioxide and carbon monoxide in the permeate stream by catalytic reaction to produce methane.

3. The reformer of any one of claims 1 and 2, wherein the reformer is adapted to receive a liquid-phase feedstock and vaporize the feedstock prior to delivery to the reforming catalyst bed.

4. The reformer of any one of claims 1-3, wherein the reforming region includes a plurality of reforming catalyst beds within the shell.

5. The reformer of any one of claims 1-4, wherein the hydrogen-selective membrane is tubular.

6. The reformer of any one of claims 1-5, wherein the reforming catalyst bed at least partially surrounds the hydrogen-selective membrane.

7. The reformer of any one of claims 1-6, wherein the amount of hydrogen in the product stream is less than a maximum available amount of hydrogen.

8. The reformer of claim 7, wherein the amount of hydrogen in the product stream is between approximately 50% and approximately 80% of the maximum available amount of hydrogen.

9. The reformer of any one of claims 1-8, wherein the reformer further includes a combustion chamber adapted to receive and combust a fuel stream with an air stream to generate heat for heating the reformer.

10. The reformer of claim 9, wherein the fuel stream is at least partially comprised of the byproduct stream.

11. The reformer of claim 10, wherein the byproduct stream contains sufficient hydrogen to provide, when combusted with air, sufficient heat to maintain the reforming catalyst bed at or above a selected operating temperature.

12. The reformer of any one of claims 9-11, wherein the reformer further includes a polishing catalyst bed located at least substantially within the combustion chamber, wherein the polishing catalyst bed includes a methanation catalyst, and further wherein the polishing catalyst bed is in fluid communication with the hydrogen purification module and is adapted to receive the permeate stream therefrom and reduce the concentration of carbon dioxide and carbon monoxide in the permeate stream by catalytic reaction to produce methane.

13. The reformer of any one of claims 9-12, wherein the combustion chamber receives air for supporting combustion from a cathode air stream discharged from a fuel cell.

14. The reformer of any one of claims 9-13, wherein the reforming feedstock is preheated prior to passage into the reforming region by heat exchange with at least one of the

product stream and an exhaust stream from the combustion chamber.

15. The reformer of any one of claims 1-14, further comprising a heater adapted to heat the reforming catalyst bed to a selected operating temperature.

16. The reformer of any one of claims 1-15, wherein the hydrogen-selective membrane further comprises carbon, with the carbon present in the hydrogen-selective membrane in a concentration of no more than 146 ppm.

17. The reformer of claim 16, wherein the hydrogen-selective membrane includes no more than 56 ppm carbon.

18. The reformer of claim 17, wherein the hydrogen-selective membrane contains less than 40 ppm carbon.

19. The reformer of any one of claims 1-18, wherein silicon is present in the hydrogen-selective membrane in a concentration of 10–15 ppm.

20. The reformer of any one of claims 1-19, wherein the hydrogen-selective membrane further contains oxygen, and further wherein the oxygen is present in the hydrogen-selective membrane in a concentration of no more than 25 ppm.

21. The reformer of any one of claims 1-20, wherein the hydrogen-selective membrane contains approximately 40 wt% copper.

22. The reformer of any one of claims 1-21, wherein the hydrogen-selective membrane is formed from an alloy containing palladium and approximately 40 wt% copper, has a thickness of 25 microns and is adapted to permit a hydrogen flux of at least 130 std. $ft^3/ft^2 \bullet hr$ through the membrane at 400° C and 100 psig hydrogen.

23. The reformer of any one of claims 1-22, wherein the reformer includes a plurality of the hydrogen-selective membranes.

24. The reformer of any one of claims 1-23, wherein the hydrogen-selective membrane includes a permeate surface and further wherein the hydrogen purification module includes a support adapted to support the permeate surface of the hydrogen-selective membrane.

25. The reformer of claim 24, wherein the support is formed from at least one of the group consisting of metal, carbon, ceramic foam, porous ceramic, microporous ceramic, porous metal, microprorous metal, metal mesh, perforated metal, metal screen, metal spring, corrosion-resistant metal, and slotted metal.

26. The reformer of any one of claims 1-25, further comprising a reforming catalyst bed downstream from the hydrogen purification module.

27. The reformer of any one of claim 1-26, wherein the at least one of a hydrocarbon and an alcohol in the reforming feedstock is selected to be nonflammable under the operating conditions of the steam reformer.

28. The reformer of claim 27, wherein the at least one of a hydrocarbon and an alcohol in the reforming feedstock is selected from the group consisting of polyhydroxyl alcohols, polyethers, ethylene glycol, propylene glycol, glycol ethers of ethylene glycol and glycol ethers of propylene glycol.

29. The reformer of claim 27, wherein the at least one of a hydrocarbon and an alcohol in the reforming feedstock has a vapor pressure of less than 100 torr at 100° C.

30. A process for producing hydrogen containing concentrations of carbon monoxide and carbon dioxide below a defined minimum level, the process comprising:

receiving a reforming feedstock containing water and at least one of a hydrocarbon and an alcohol;

delivering the reforming feedstock to a reforming catalyst bed to produce a reforming product stream comprising hydrogen, carbon monoxide and carbon dioxide; and

passing the reforming product stream to a hydrogen purification module containing a hydrogen-selective membrane to produce a permeate stream comprising the reforming

product stream which passes through the membrane, and a byproduct stream comprising the reforming product stream not passed through the membrane, wherein the hydrogen-selective membrane comprises palladium, copper and silicon, and further wherein the silicon is present in the membrane in a concentration of 10–39 ppm.

31. The process of claim 30, further comprising passing the permeate stream through a polishing catalyst bed containing a methanation catalyst to convert at least a substantial portion of the carbon monoxide and the carbon dioxide in the permeate stream into methane.

32. The process of any one of claims 30 and 31, wherein the receiving step includes receiving a liquid-phase reforming feedstock, and the process further comprises vaporizing the reforming feedstock prior to delivering the feedstock to the reforming catalyst bed.

33. The process of any one of claims 30-32, further comprising preheating the reforming feedstock prior to the delivering step by heat exchange with at least one of the product stream and an exhaust stream from a combustion chamber.

34. The process of any one of claims 30-33, further comprising combusting the byproduct stream with air to heat and maintain the reforming catalyst bed within a selected operating temperature range.

35. The process of any one of claims 30-34, wherein between 50 % and 80 % of a maximum available amount of hydrogen is recovered as the reforming product stream and the remaining amount of the maximum available amount of hydrogen is withdrawn as a portion of the byproduct stream.

36. The process of any one of claims 30-35, wherein the remaining amount of hydrogen in the byproduct stream is mixed with air and combusted to heat the reforming catalyst bed.

37. The process of any one of claims 30-36, wherein the hydrogen-selective membrane contains 10–15 ppm silicon.

38. The process of any one of claims 30-36, wherein the hydrogen-selective membrane further contains carbon, with the carbon being present in the hydrogen-selective membrane in a concentration of no more than 146 ppm carbon.

39. The process of claim 38, wherein the hydrogen-selective membrane contains less than 56 ppm carbon.

40. The process of claim 39, wherein the hydrogen-selective membrane contains less than 40 ppm carbon.

41. The process of any one of claims 30-40, wherein the hydrogen-selective membrane further contains oxygen, and further wherein the oxygen is present in the hydrogen-selective membrane in a concentration of no more than 25 ppm.

42. The process of any one of claims 30-41, wherein the hydrogen-selective membrane contains approximately 40 wt% copper.

43. A hydrogen purification device, comprising:

an enclosure defining an internal compartment; wherein the enclosure includes at least one input port through which a mixed gas stream containing hydrogen gas and other gases is delivered to the enclosure, at least one product output port through which a permeate stream containing at least substantially pure hydrogen gas is removed from the enclosure, and at least one byproduct output port through which a byproduct stream containing at least a substantial portion of the other gases is removed from the enclosure; and

at least one hydrogen-selective membrane within the compartment, wherein the at least one hydrogen-selective membrane includes a first surface adapted to be contacted by the mixed gas stream and a permeate surface generally opposed to the first surface, wherein the permeate stream is formed from a portion of the mixed gas stream that passes through the at least one hydrogen-selective membrane to the permeate surface, and the byproduct stream is formed from a portion of the mixed gas stream that does not pass through the at least one hydrogen-selective membrane, wherein the membrane is substantially comprised of a primary component selected from a group consisting essentially of palladium and a palladium alloy, and further wherein the membrane further comprises a secondary component consisting of

silicon, with the silicon present in the membrane in a concentration of approximately 10–39 ppm.

44. The device of claim 43, wherein the silicon present in the membrane is in a concentration of 10–15 ppm.

45. The device of claim 43, wherein the silicon present in the membrane is in a concentration of 10-39 ppm.

46. The device of any one of claims 43-45, wherein the secondary component forms an alloy with the primary component.

47. The device of any one of claims 43-46, wherein the primary component includes an alloy of palladium and copper.

48. The device of any one of claims 43-47, wherein the primary component includes an alloy containing palladium and approximately 40 wt% copper.

49. The device of any one of claims 43-48, wherein the membrane further comprises carbon, with the carbon being present in the membrane in a concentration of no more than 146 ppm.

50. The device of claim 49, wherein the membrane further comprises carbon in a concentration of no more than 56 ppm.

51. The device of any one of claims 43-50, further comprising a support adapted to support the at least one hydrogen-selective membrane.

52. The device of claim 51, wherein the at least one hydrogen-selective membrane is formed upon the support.

53. The device of any one of claims 51 and 52, wherein the support is adapted to support the permeate surface of the at least one hydrogen-selective membrane.

54. The device of any one of claims 51 and 53, wherein the support physically contacts and extends generally along the permeate surface of the at least one hydrogen-selective membrane.

55. The device of any one of claims 53 and 54, wherein the support engages, but is not bonded to, the permeate surface of the at least one hydrogen-selective membrane.

56. The device of any one of claims 51-55, wherein the support is formed from a porous material.

57. The device of any one of claims 51-56 wherein the support includes at least one mesh screen.

58. The device of any one of claims 43-57, wherein the at least one hydrogen-selective membrane is mounted on a frame that is housed within the enclosure.

59. The device of any one of claims 51-58, wherein the support includes a coating that is thermodynamically stable with respect to decomposition in the presence of hydrogen and which is adapted to prevent intermetallic diffusion between the support and the membrane.

60. The device of any one of claims 43-59, wherein the enclosure includes a plurality of the hydrogen-selective membranes.

61. The device of any one of claims 43-60, wherein the device includes at least one membrane envelope formed from a pair of the hydrogen-selective membranes oriented such that the pair of hydrogen-selective membranes are spaced-apart from each other with their permeate surfaces generally facing each other to define a harvesting conduit extending therebetween, and further wherein the permeate stream is formed from the portion of the mixed gas stream that passes through the membranes to the harvesting conduit, with the remaining portion of the mixed gas stream which remains on the first surface of the membranes forming at least a portion of the byproduct stream.

62. The device of claim 61, wherein the at least one membrane envelope includes a support within the harvesting conduit and adapted to support the pair of hydrogen-selective membranes, wherein the support includes a pair of generally opposed surfaces which are adapted to provide support to a respective one of the permeate surfaces of the pair of hydrogen-selective membranes.

63. The device of any one of claims 61 and 62, wherein the enclosure includes a plurality of membrane envelopes.

64. The device of claim 63, wherein the hydrogen purification device includes a plurality of gas transport conduits interconnecting the plurality of membrane envelopes to selectively deliver the mixed gas stream to the first surfaces of the membranes, remove the permeate stream from the harvesting conduit, and remove the byproduct stream.

65. The device of any one of claims 43-64, in combination with a fuel cell stack adapted to receive at least a portion of the permeate stream.

66. The device of any one of claims 43-65, in combination with a fuel processor having at least one hydrogen-producing region adapted to produce the mixed gas stream.

67. The device of claim 66, wherein the fuel processor is adapted to produce the mixed gas stream by steam reforming a feed stream containing water and at least one carbon-containing feedstock.

68. The device of claim 67, in further combination with a polishing assembly adapted to reduce the concentration of any carbon monoxide present in the permeate stream.

69. In a hydrogen purification device that is adapted to be operated at a temperature of at least 200° C and a pressure of at least 50 psi and which includes an enclosure with an internal, at least substantially fluid-tight compartment having at least one inlet, at least one outlet, and containing at least one hydrogen-selective metal membrane adapted to separate a mixed gas stream containing hydrogen gas and other gases into a hydrogen-rich stream containing at least substantially hydrogen gas and a byproduct stream containing at least a substantial portion of the other gases, the improvement comprising: the membrane being at least substantially comprised of an alloy of palladium, copper and silicon, with the silicon being present in the alloy in a concentration of 10–39 ppm.

70. The device of claim 69, wherein the alloy comprises 10–15 ppm silicon.

71. The device of any one of claims 69 and 70, wherein the alloy further comprises carbon, with the carbon being present in the alloy in a concentration of no more than 146 ppm.

72. The device of claim 71, wherein the alloy further comprises carbon, with the carbon being present in the alloy in a concentration of no more than 56 ppm.

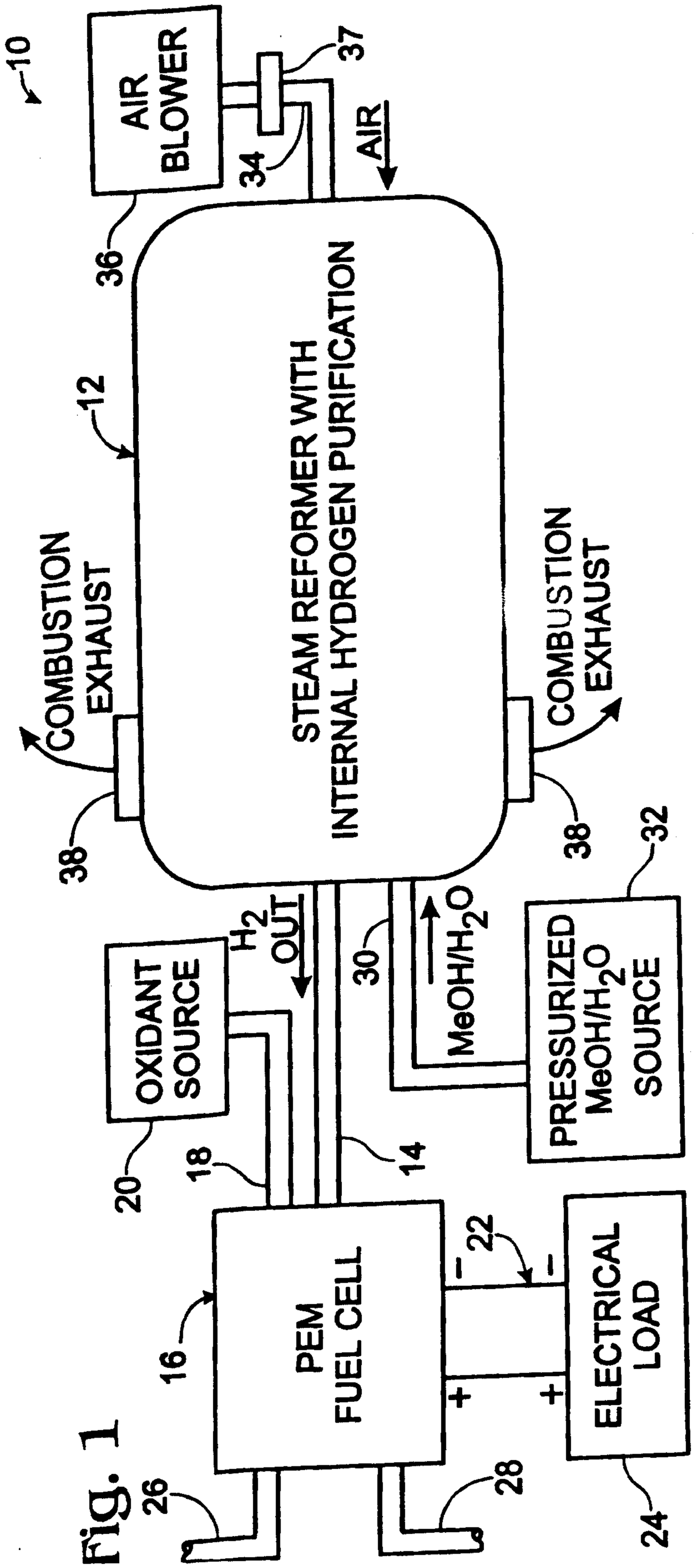
73. The device of any one of claims 69-72, wherein the alloy comprises approximately 40 wt% copper.

74. The device of any one of claims 69-73, wherein the alloy includes at least one additional component other than palladium, copper and silicon.

75. The device of any one of claims 69-74, wherein the membrane includes at least one component in addition to the alloy.

76. The device of any one of claims 69-75, in combination with a fuel processor that is adapted to produce the mixed gas stream.

77. The device of any one of claims 69-76, in further combination with a fuel cell stack adapted to receive at least a portion of the hydrogen-rich stream.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COMBUSTION EXHAUST
STEAM REFORMER WITH INTERNAL HYDROGEN PURIFICATION
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$MeOH/H_2O$
PRESSURIZED $MeOH/H_2O$ SOURCE
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Fig. 1

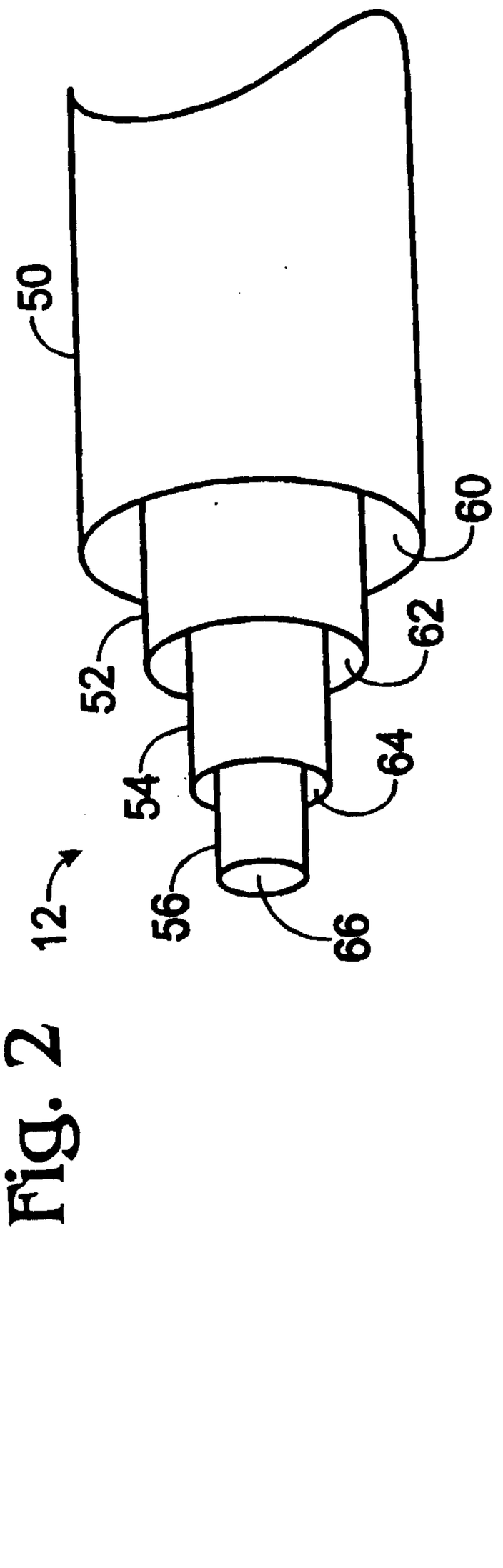
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Fig. 2

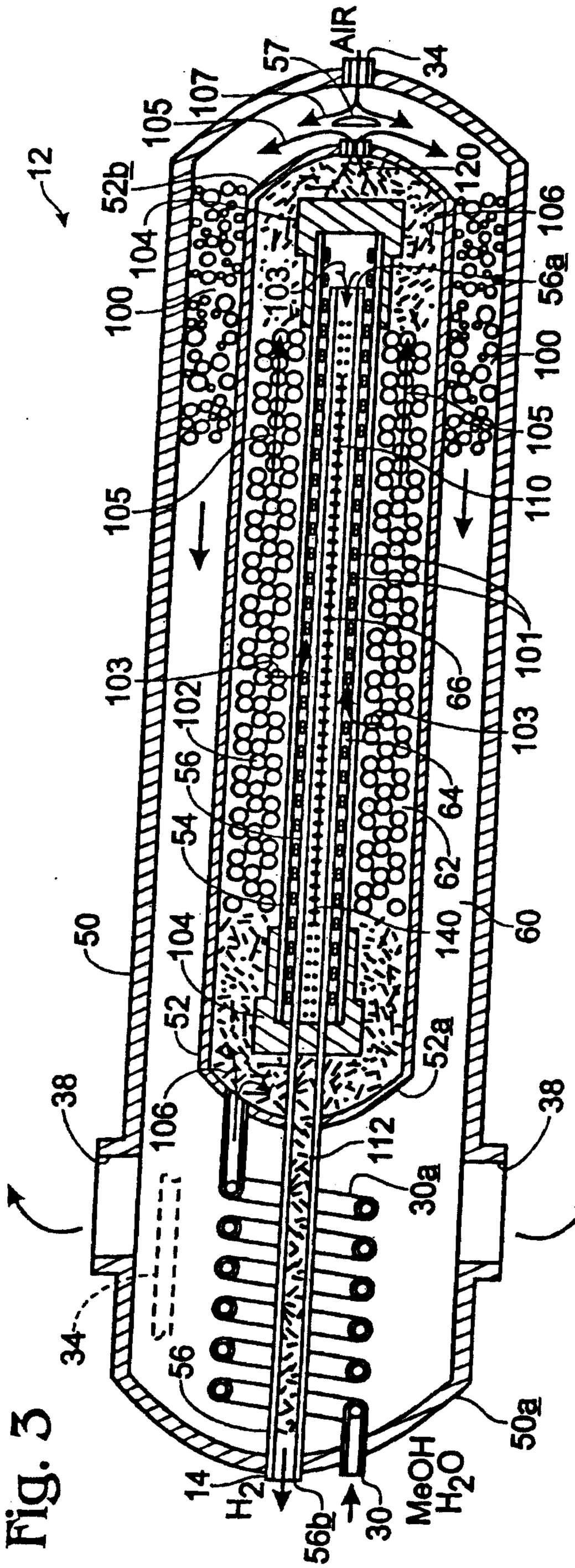
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Fig. 3

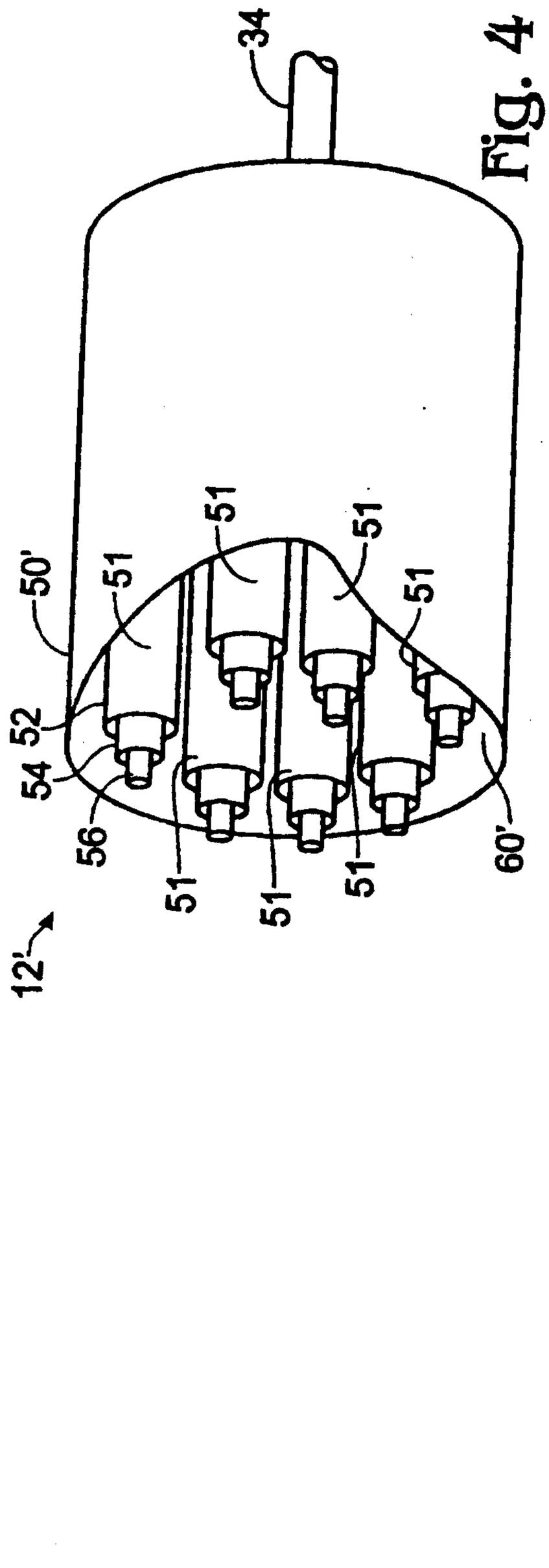
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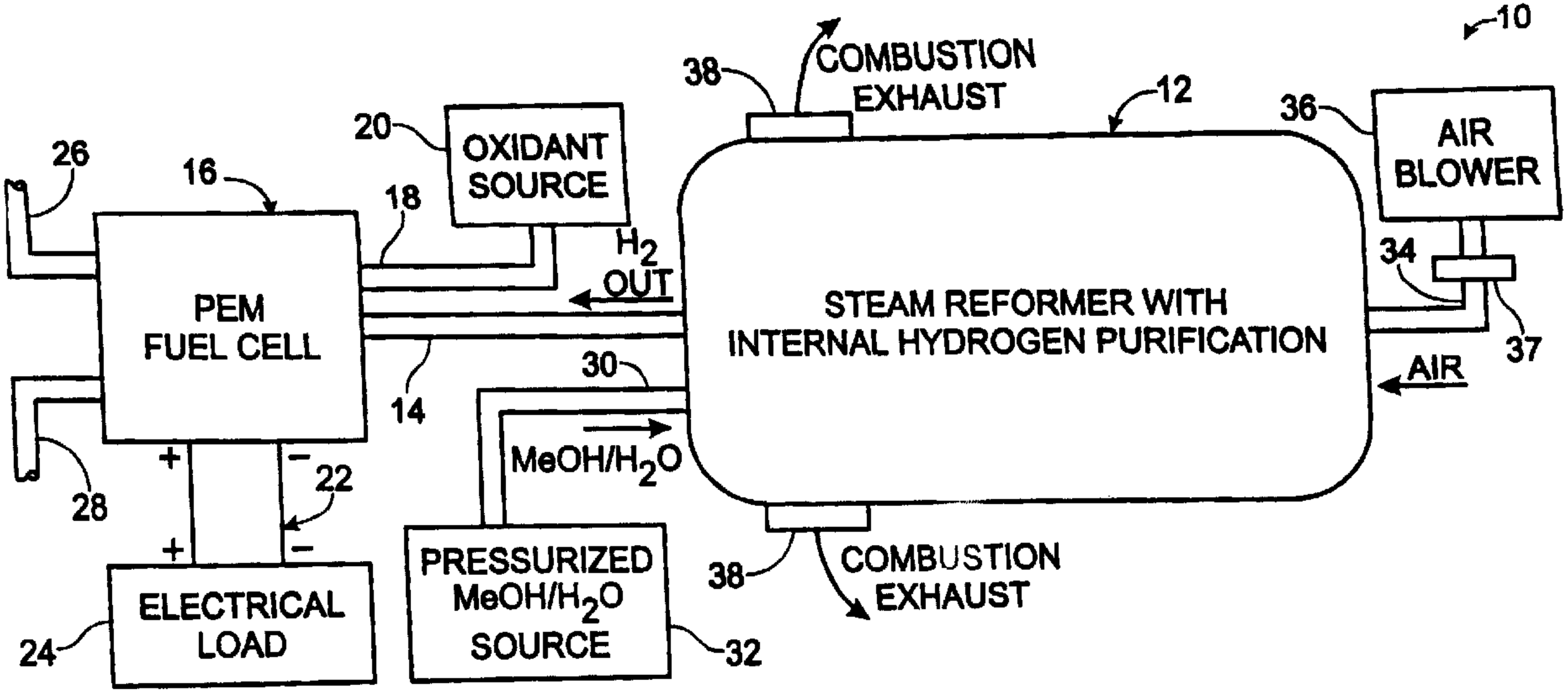
Fig. 4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COMBUSTION EXHAUST
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AIR BLOWER
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H_2 OUT
34
PEM FUEL CELL
STEAM REFORMER WITH INTERNAL HYDROGEN PURIFICATION
37
AIR
30
14
MeOH/H_2O
+
−
22
28
+
−
ELECTRICAL LOAD
PRESSURIZED MeOH/H_2O SOURCE
38
COMBUSTION EXHAUST
24
32