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(54) **HIGH TEMPERATURE FUEL CELL SYSTEM AND METHOD OF OPERATING THE SAME**

14, 2008, now Pat. No. 7,704,618, which is a division of application No. 11/002,681, filed on Dec. 3, 2004, now Pat. No. 7,422,810.

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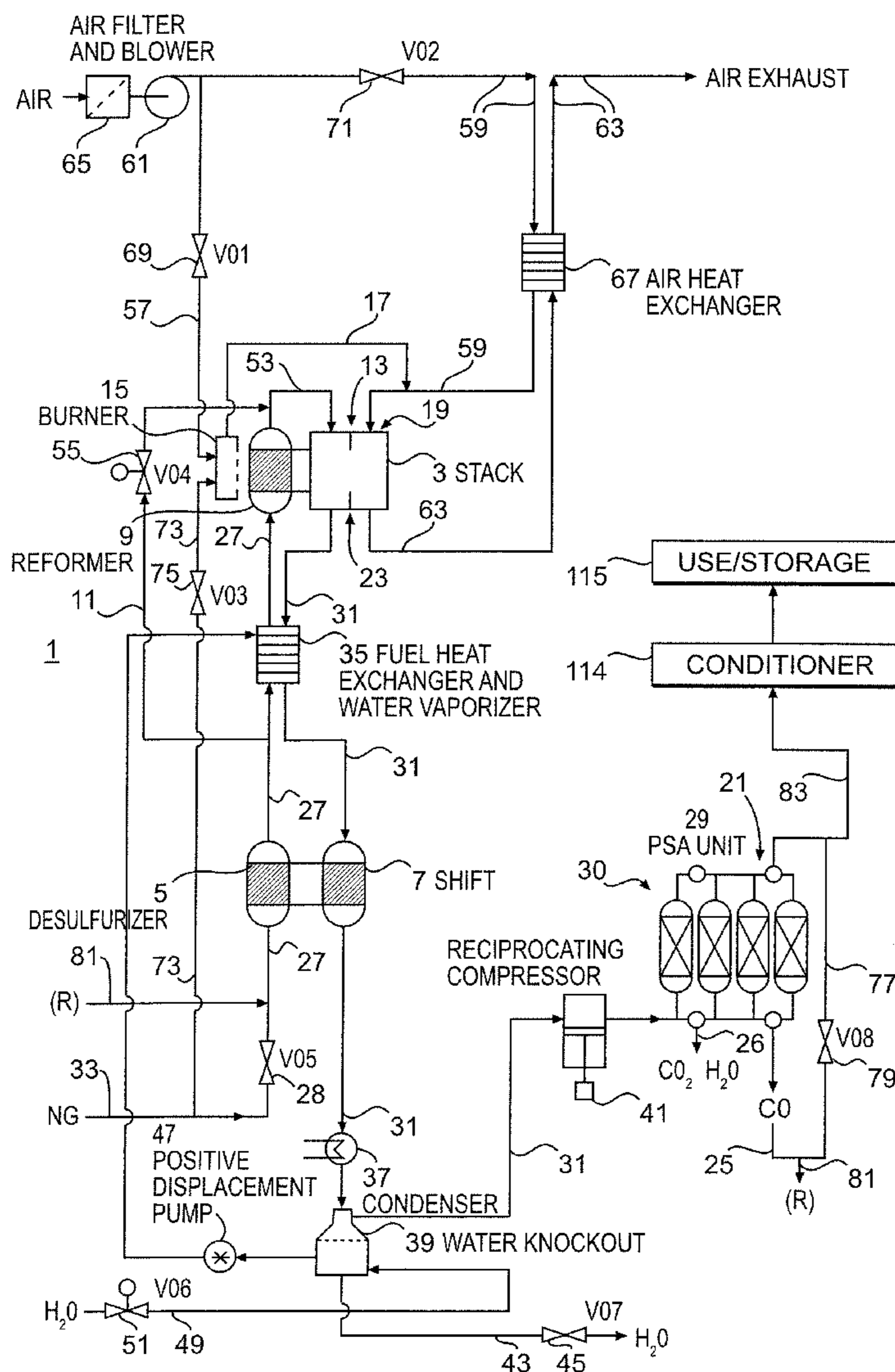
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(57) **ABSTRACT**

Related U.S. Application Data

(60) Continuation of application No. 12/765,732, filed on Apr. 22, 2010, now Pat. No. 7,901,814, which is a division of application No. 12/222,712, filed on Aug.

A high temperature fuel cell stack system, such as a solid oxide fuel cell system, with an improved balance of plant efficiency includes a thermally integrated reformer, combustor and the fuel cell stack.



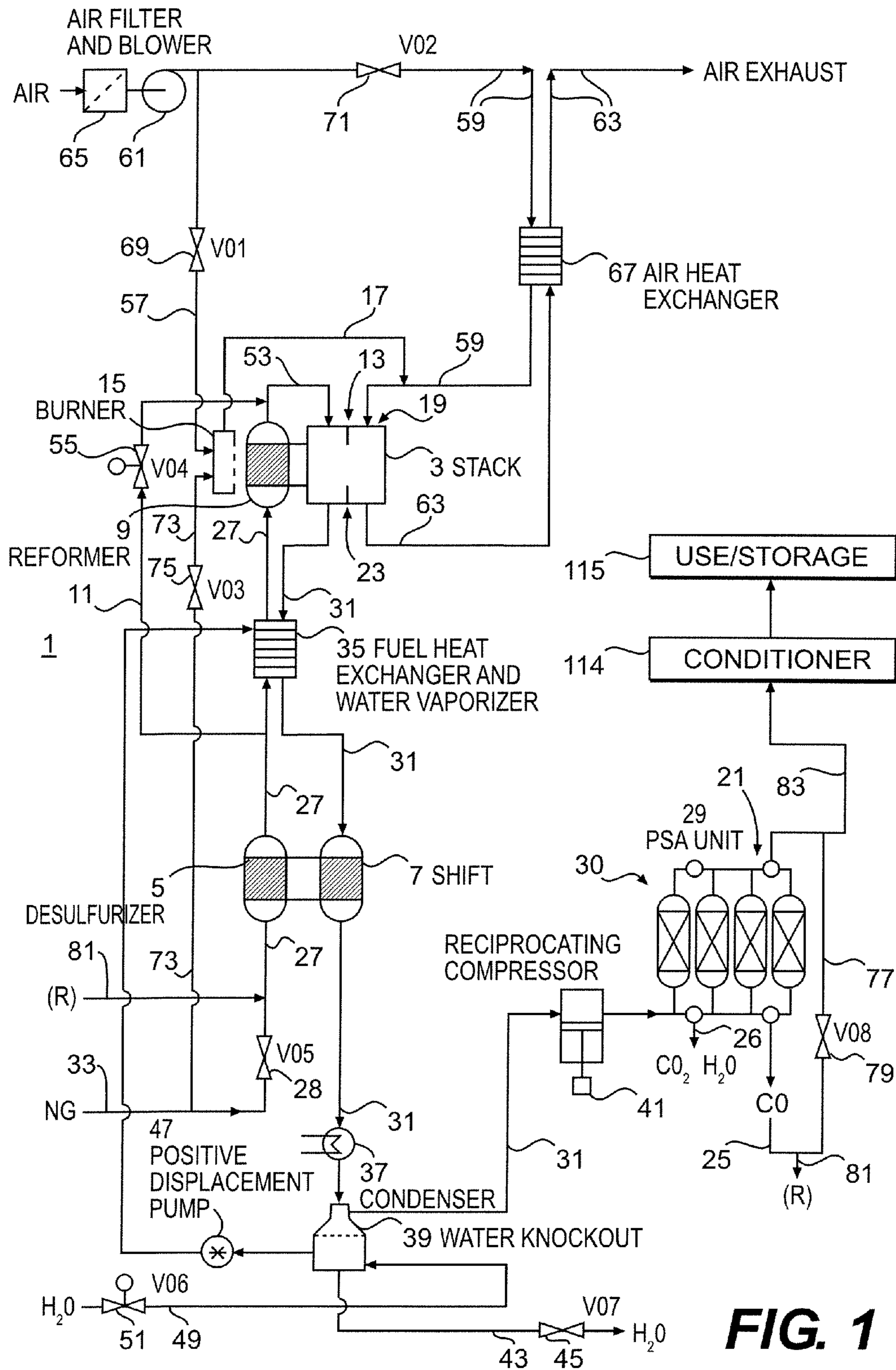


FIG. 1

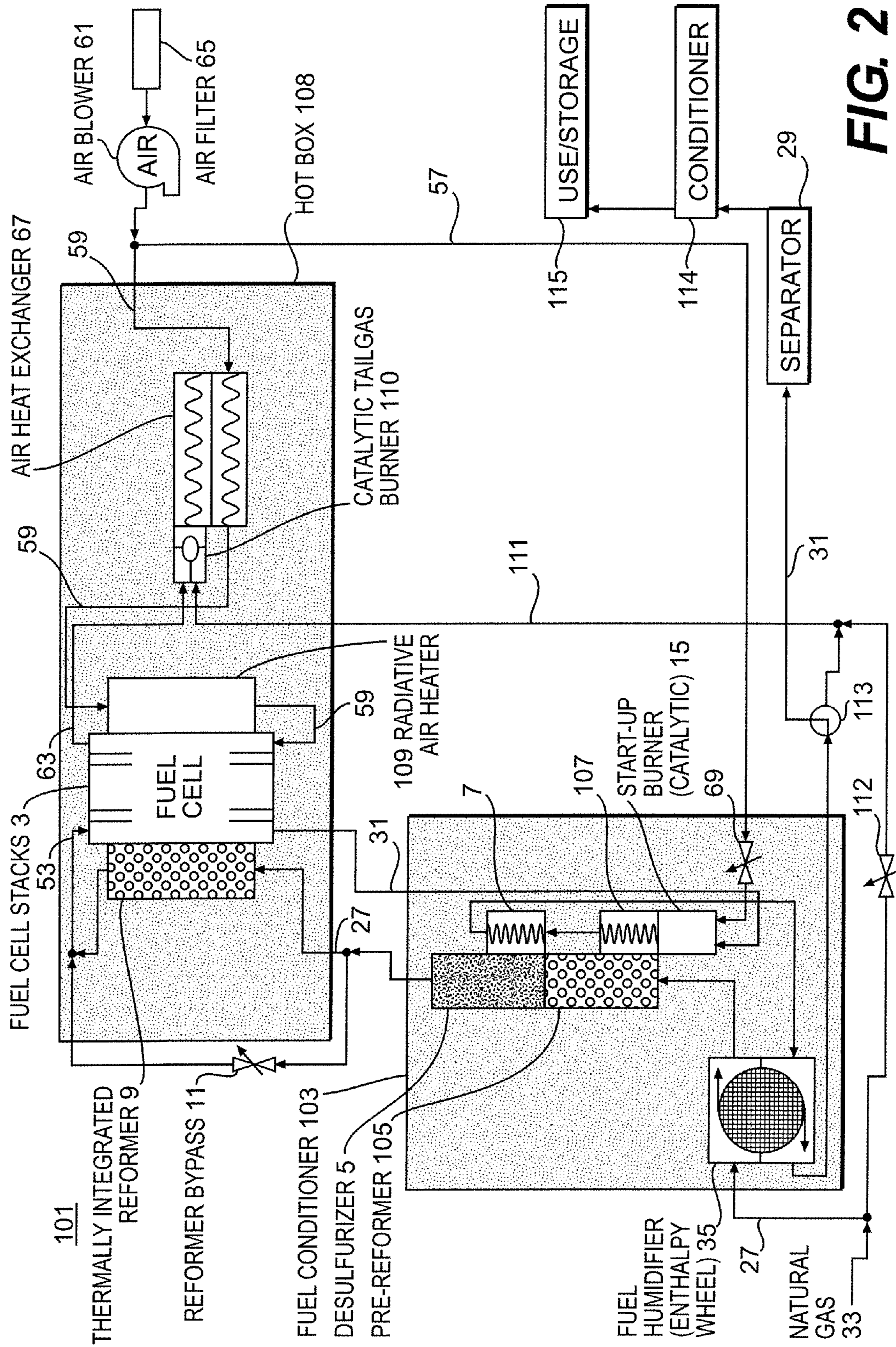


FIG. 2

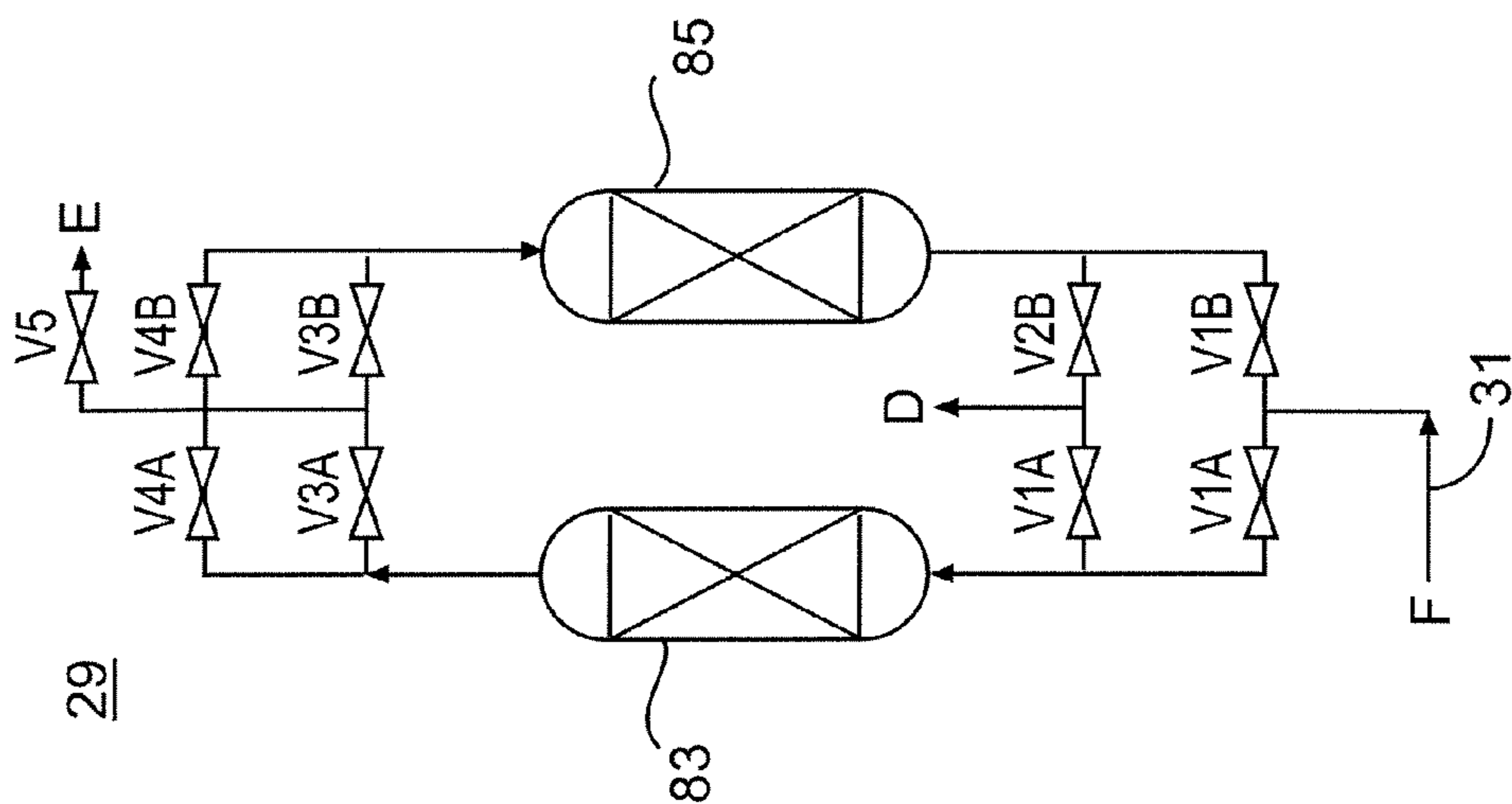


FIG. 6

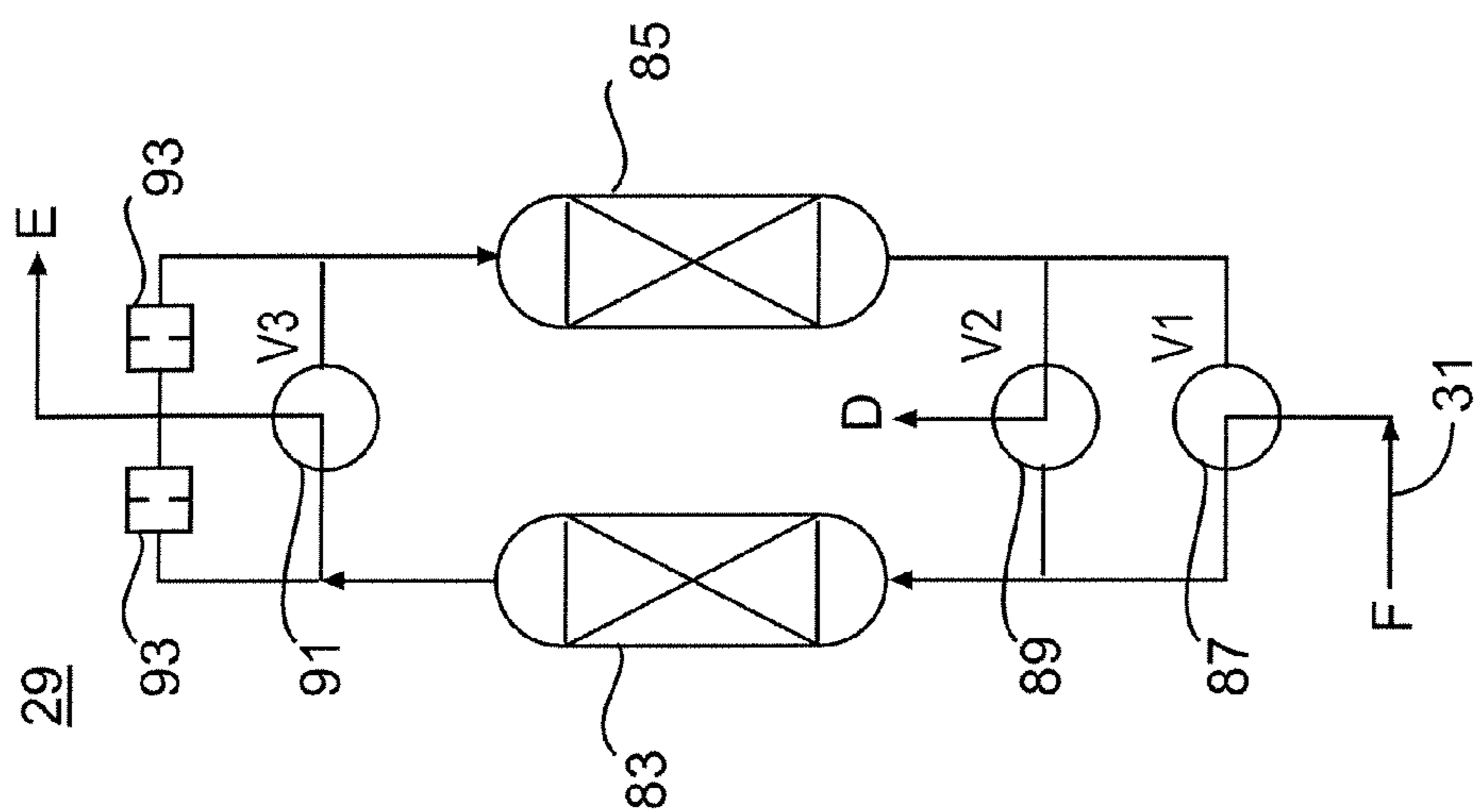


FIG. 3

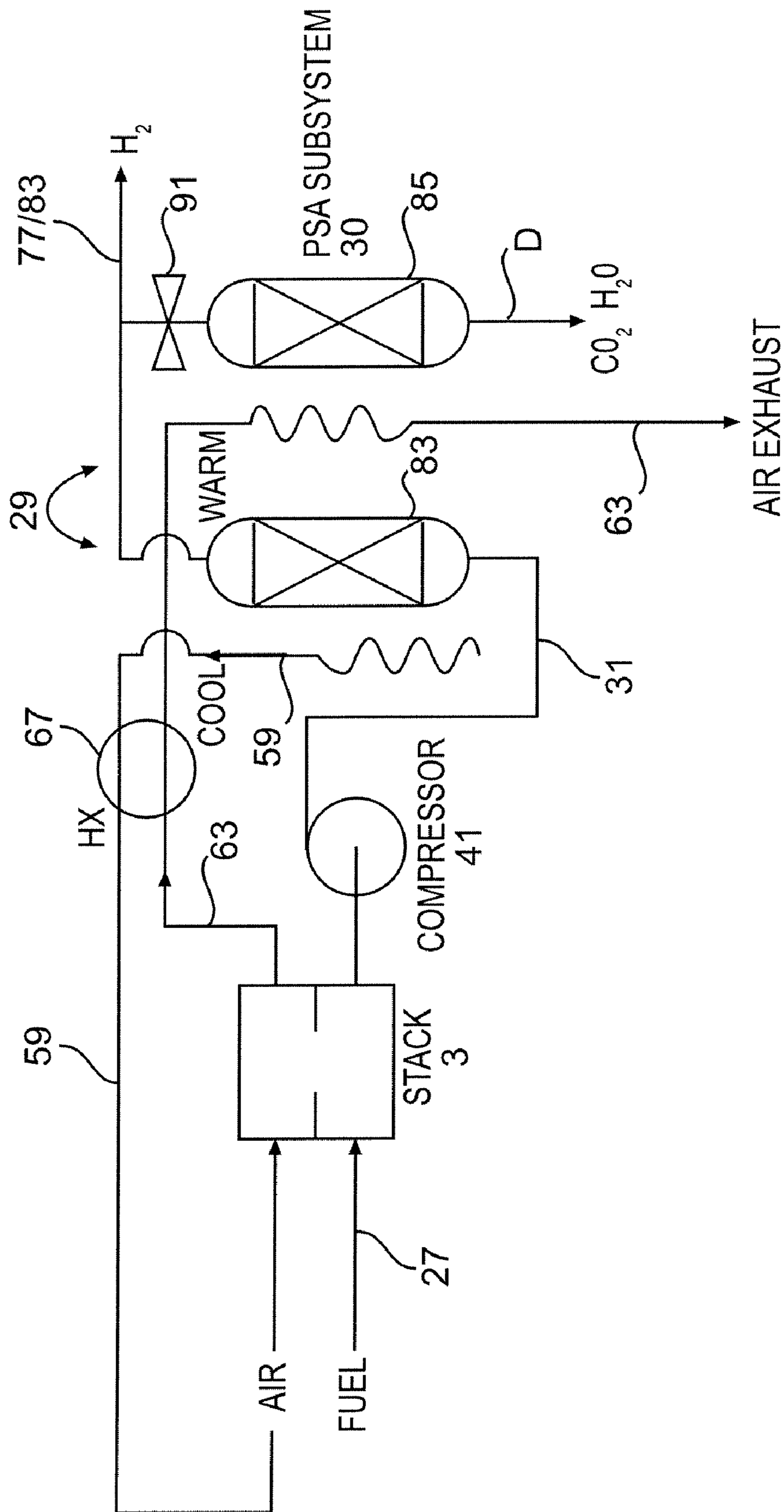


FIG. 4

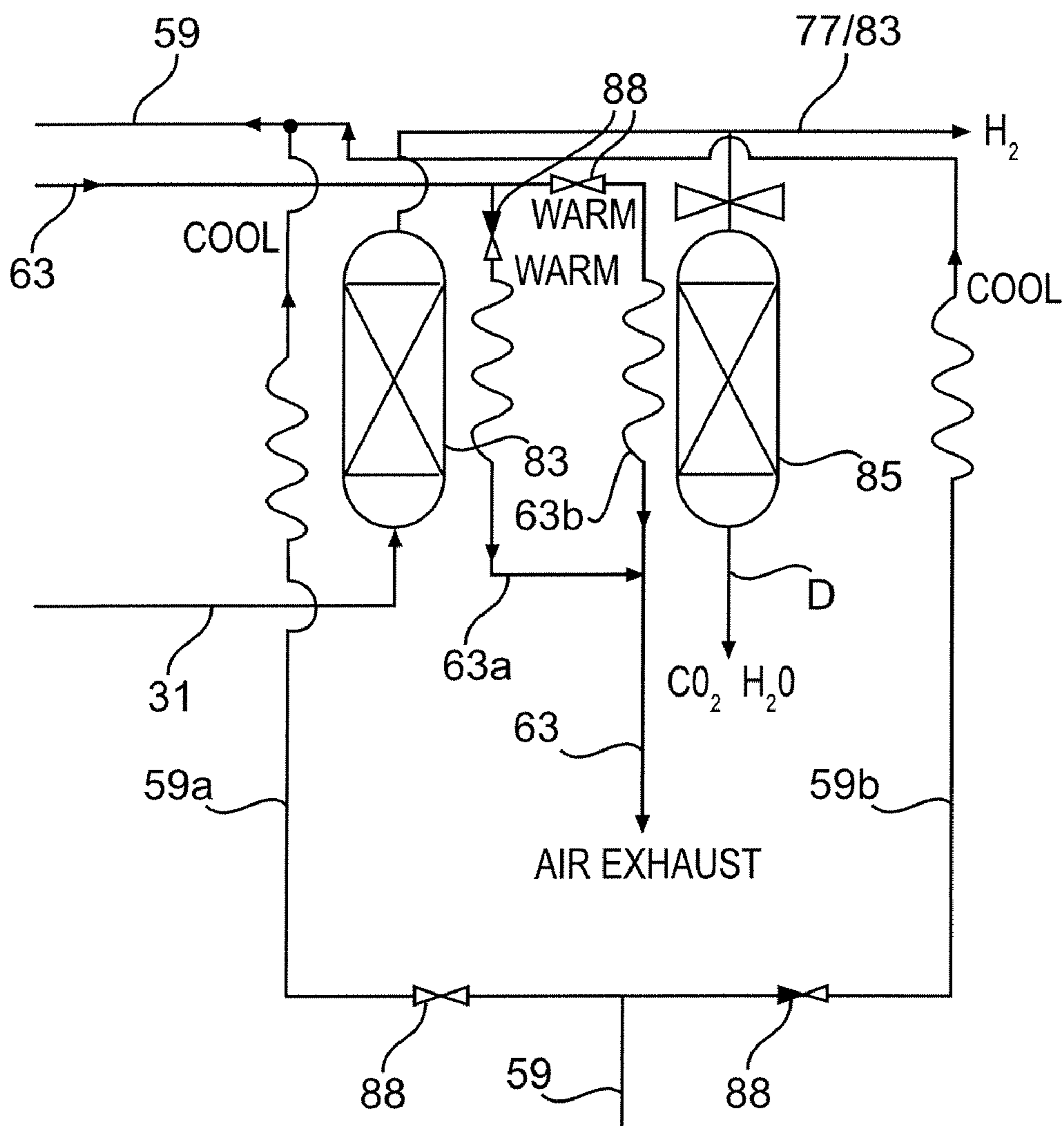


FIG. 5

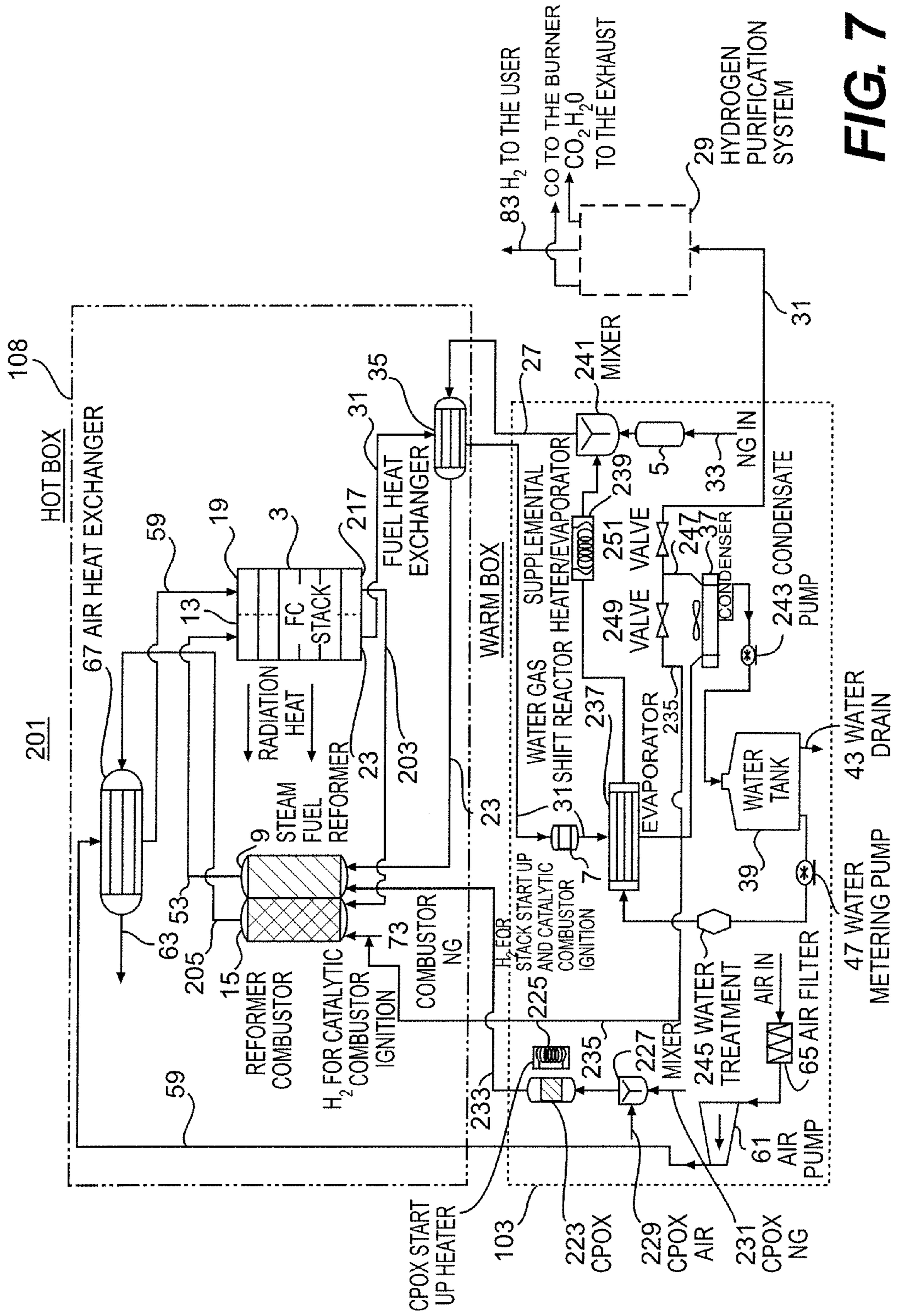
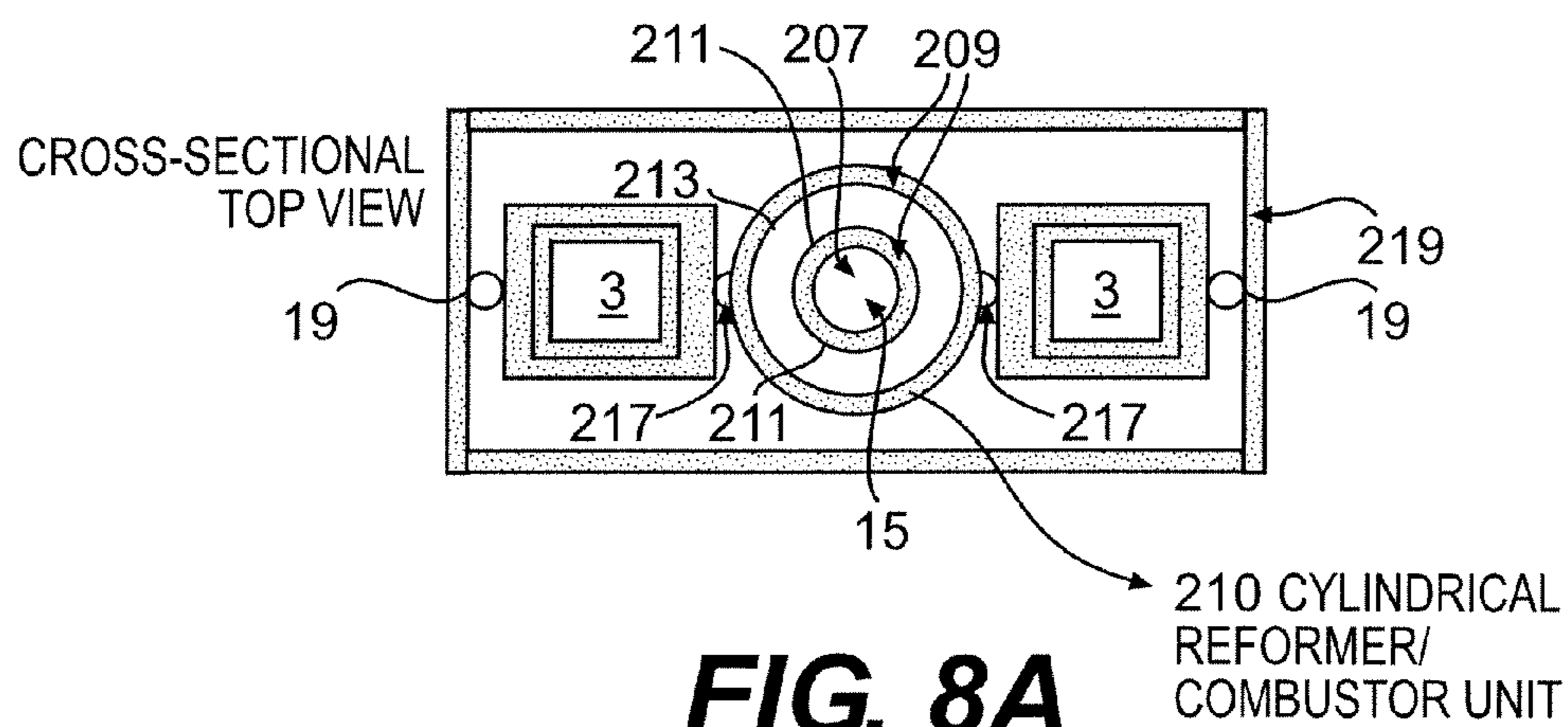
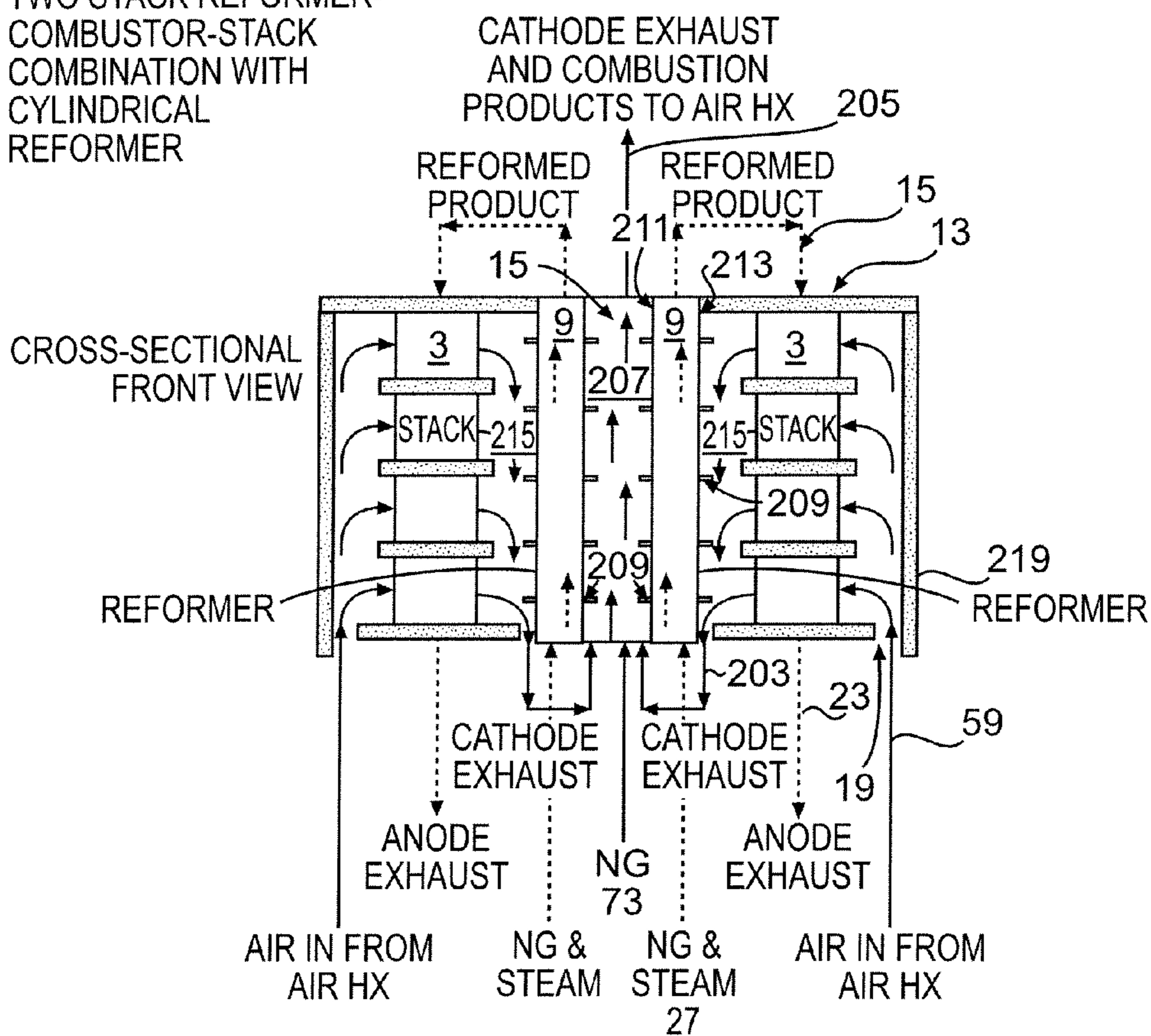
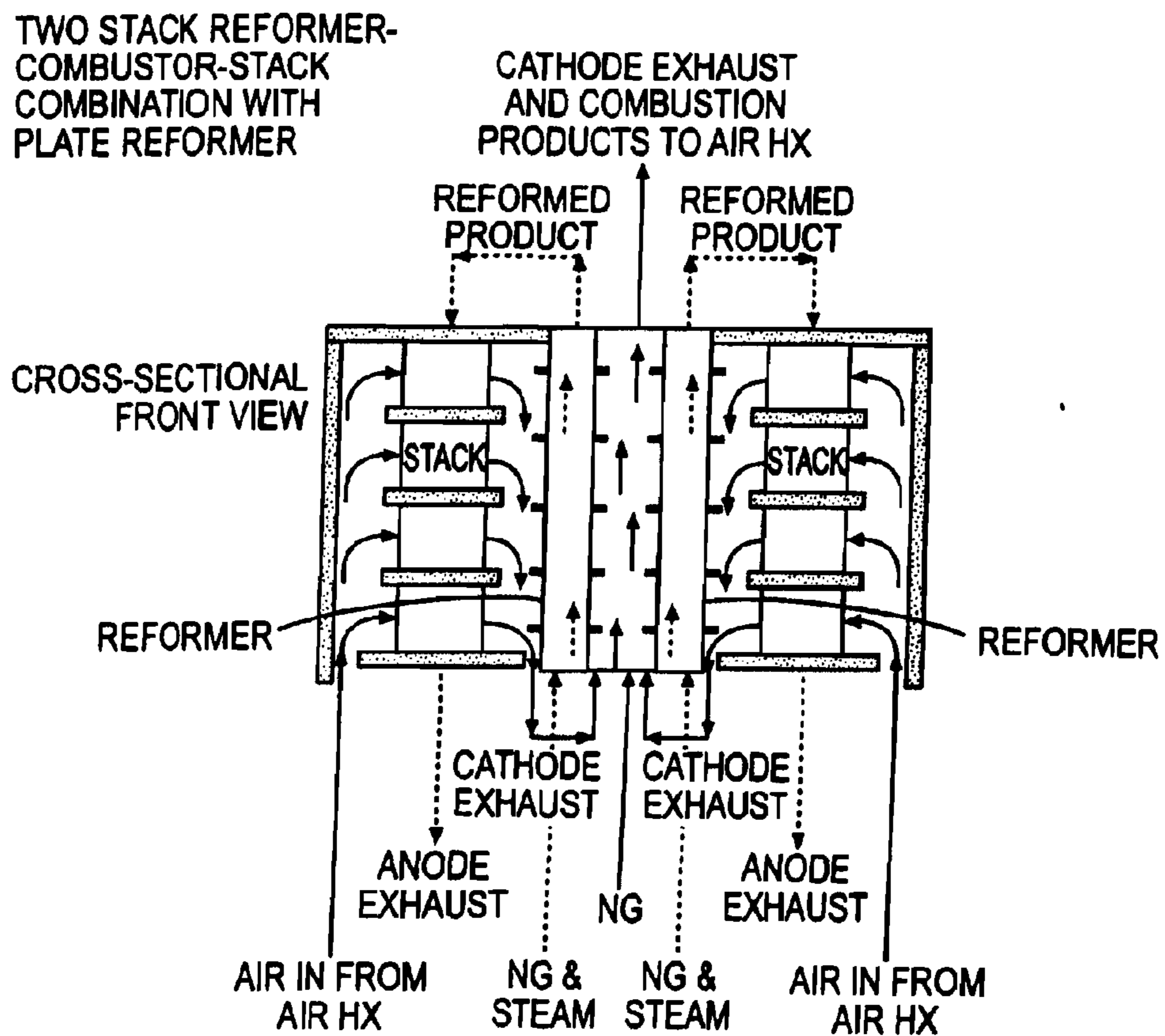
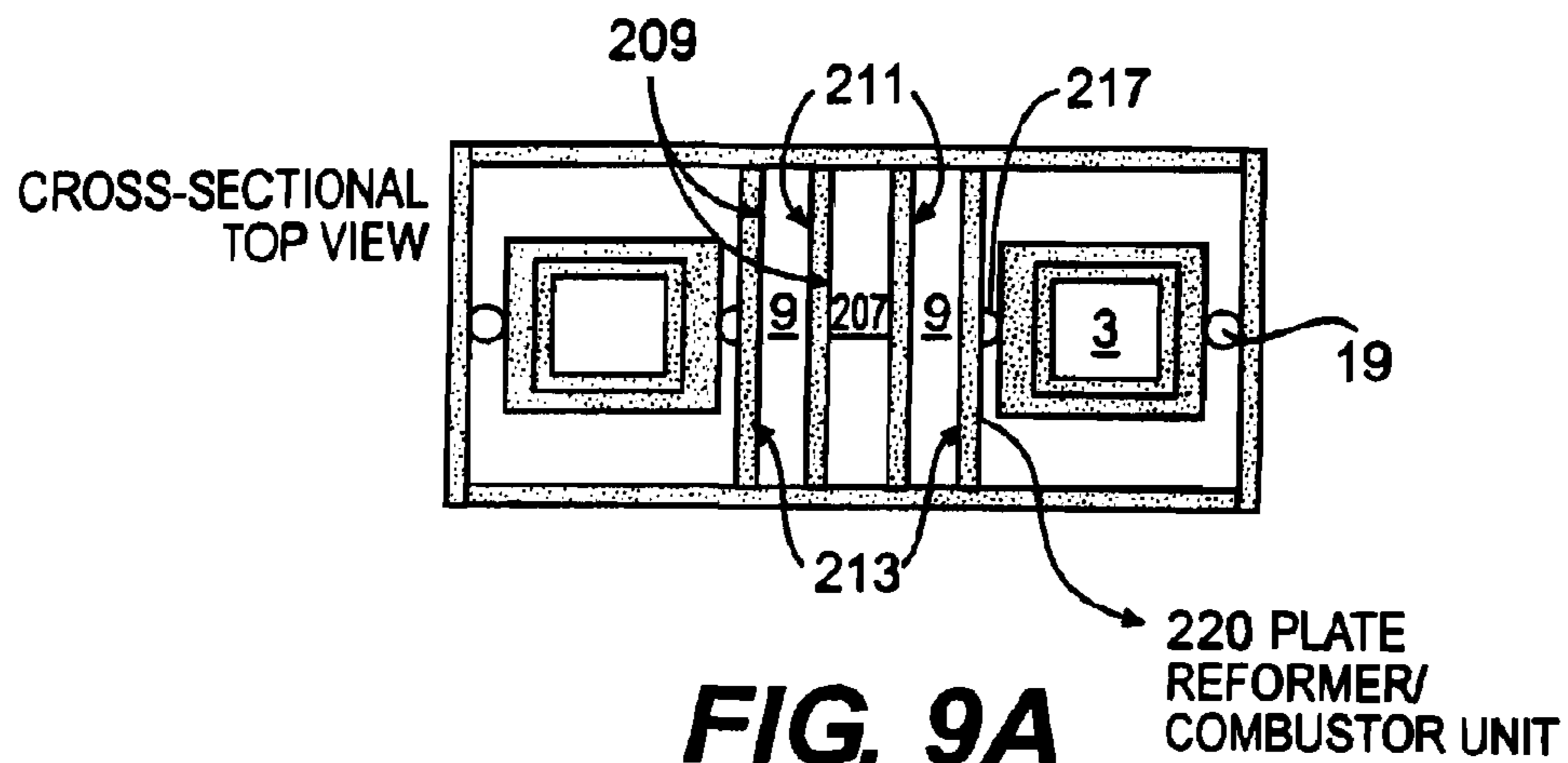


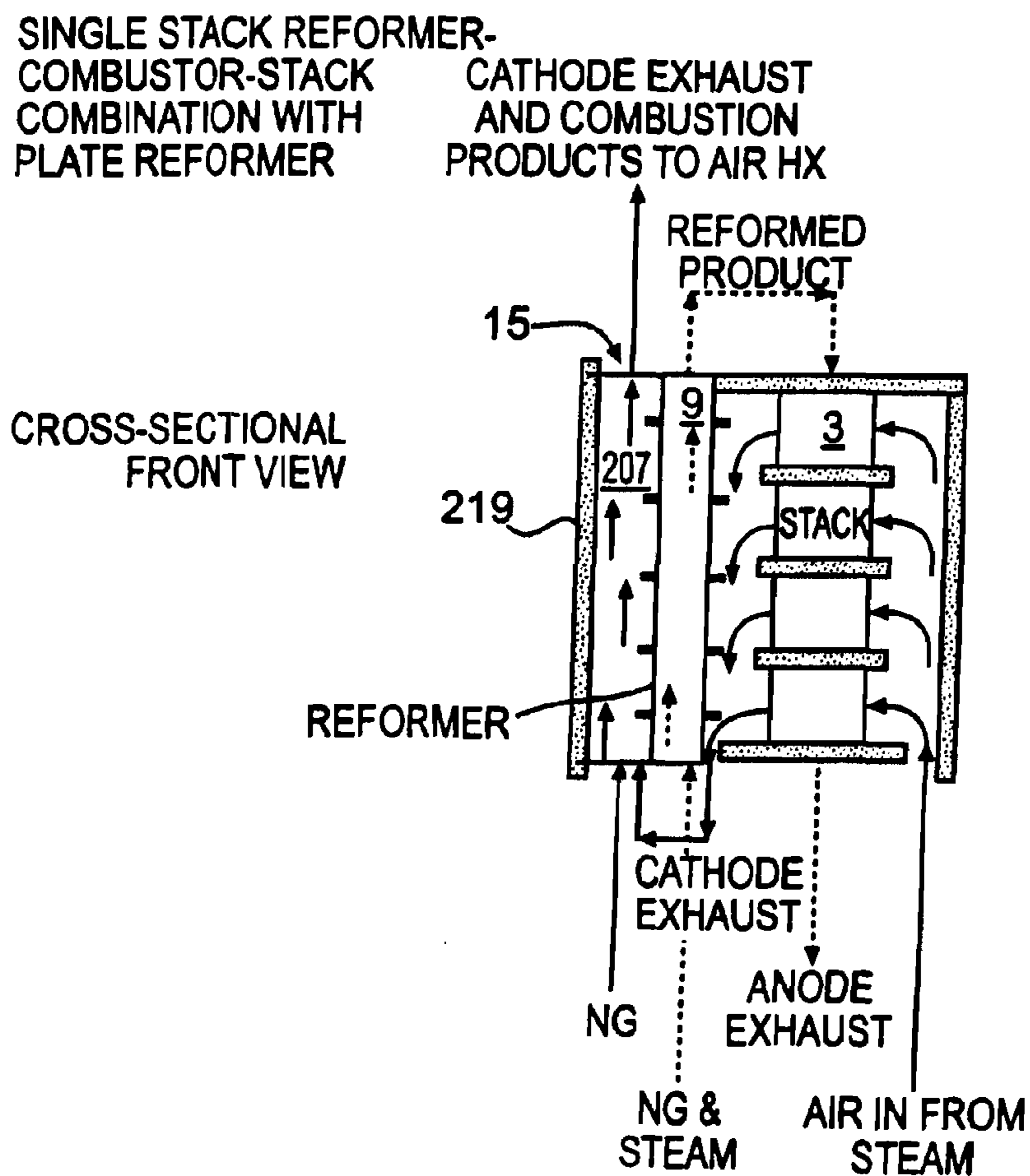
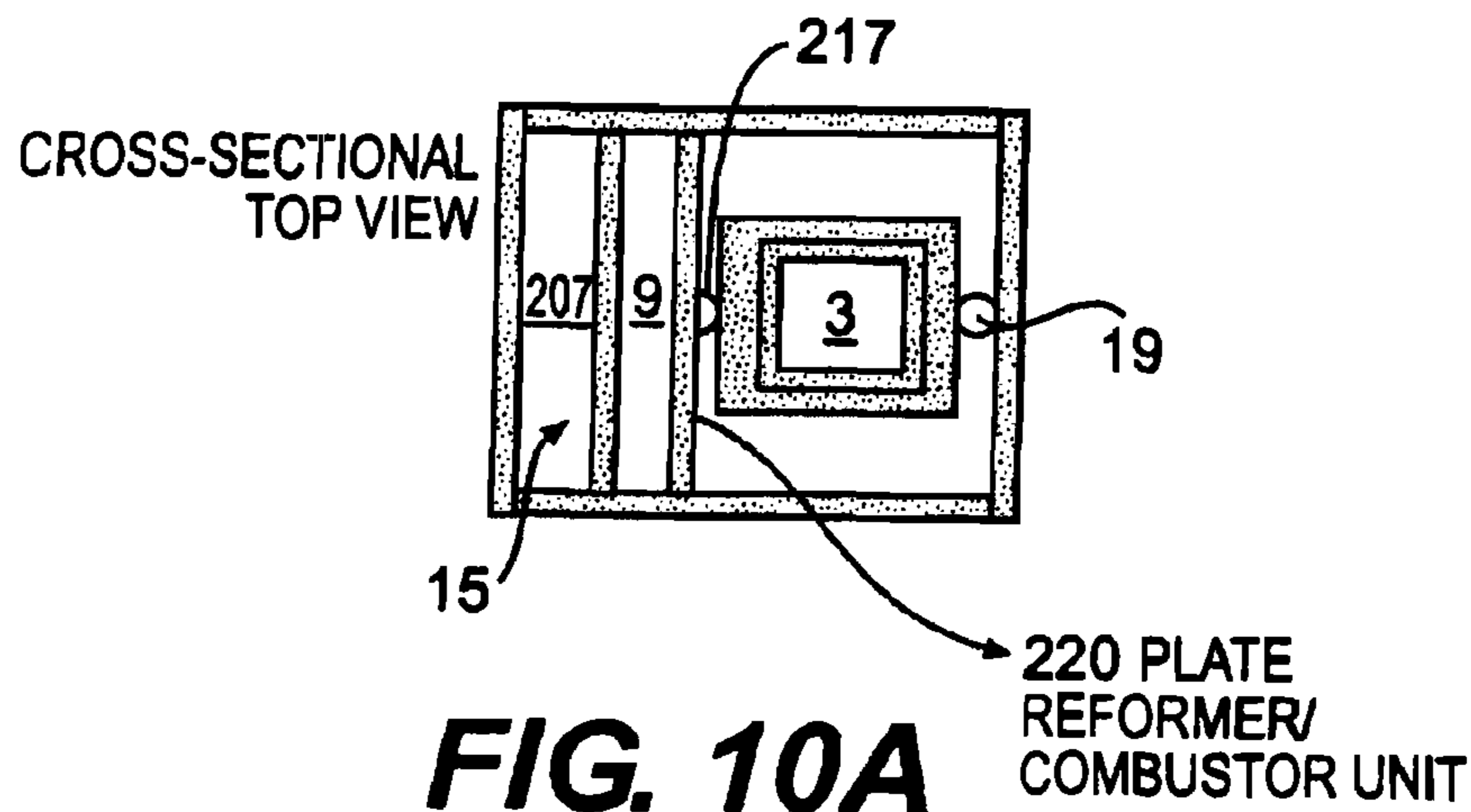
FIG. 7



TWO STACK REFORMER-COMBUSTOR-STACK COMBINATION WITH CYLINDRICAL REFORMER







HIGH TEMPERATURE FUEL CELL SYSTEM AND METHOD OF OPERATING THE SAME

[0001] This application is a continuation application of U.S. application Ser. No. 12/765,732, filed Apr. 22, 2010, which is a divisional application of U.S. application Ser. No. 12/222,712, filed Aug. 14, 2008, now U.S. Pat. No. 7,704,618, issued Apr. 27, 2010, which is a divisional application of U.S. application Ser. No. 11/002,681, filed Dec. 3, 2004, now U.S. Pat. No. 7,422,810, issued Sep. 9, 2009, which claims the benefit of priority of U.S. provisional application 60/537,899 filed on Jan. 22, 2004 and 60/552,202 filed on Mar. 12, 2004, all of which are incorporated herein by reference in their entirety.

BACKGROUND OF THE INVENTION

[0002] The present invention is generally directed to fuel cells and more specifically to high temperature fuel cell systems and their operation.

[0003] Fuel cells are electrochemical devices which can convert energy stored in fuels to electrical energy with high efficiencies. High temperature fuel cells include solid oxide and molten carbonate fuel cells. These fuel cells may operate using hydrogen and/or hydrocarbon fuels. There are classes of fuel cells, such as the solid oxide regenerative fuel cells, that also allow reversed operation, such that oxidized fuel can be reduced back to unoxidized fuel using electrical energy as an input.

BRIEF SUMMARY OF THE INVENTION

[0004] The preferred aspects of present invention provide a high temperature fuel system, such as a solid oxide fuel cell system, with an improved balance of plant efficiency. The system includes a thermally integrated unit including a reformer, combustor and the fuel cell stack.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIGS. 1, 2 and 7 are schematics of fuel cell systems according to preferred embodiments of the present invention.

[0006] FIGS. 3 and 6 are schematics of PSA gas separation devices according to the preferred embodiments of the present invention.

[0007] FIG. 4 is a schematic of a fuel cell system according to the fifth preferred embodiment of the present invention.

[0008] FIG. 5 shows the details of the system of FIG. 4.

[0009] FIGS. 8A and 8B are schematics of integrated cylindrical reformer, combustor and stack unit for a system with two stacks.

[0010] FIGS. 9A and 9B are schematics of integrated plate type reformer, combustor and stack unit for a system with two stacks.

[0011] FIGS. 10A and 10B are schematics of integrated plate type reformer, combustor and stack unit for a single stack system.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] FIG. 1 illustrates a fuel cell system 1 according to the preferred embodiments of the present invention. Preferably, the system 1 is a high temperature fuel cell stack system, such as a solid oxide fuel cell (SOFC) system or a molten carbonate fuel cell system. The system 1 may be a regenera-

tive system, such as a solid oxide regenerative fuel cell (SORFC) system which operates in both fuel cell (i.e., discharge) and electrolysis (i.e., charge) modes or it may be a non-regenerative system which only operates in the fuel cell mode.

[0013] The system 1 contains a high temperature fuel cell stack 3. The stack may contain a plurality of SOFCs, SORFCs or molten carbonate fuel cells. Each fuel cell contains an electrolyte, an anode electrode on one side of the electrolyte in an anode chamber, a cathode electrode on the other side of the electrolyte in a cathode chamber, as well as other components, such as separator plates/electrical contacts, fuel cell housing and insulation. In a SOFC operating in the fuel cell mode, the oxidizer, such as air or oxygen gas, enters the cathode chamber, while the fuel, such as hydrogen or hydrocarbon fuel, enters the anode chamber. Any suitable fuel cell designs and component materials may be used.

[0014] The system 1 contains any one or more of the following elements, either alone or in any suitable combination. In a first embodiment, the system 1 contains a desulfurizer 5 and a water-gas shift reactor 7 that are thermally integrated with each other. The waste heat from the reactor 7 is used to heat the desulfurizer 5 to its operating temperature, thus reducing or eliminating the need for a separate desulfurizer heater.

[0015] In a second embodiment, the system 1 contains a hydrocarbon fuel reformer 9 and a hydrocarbon fuel by-pass line 11 fluidly connected to the fuel inlet 13 of the high temperature fuel cell stack 3. The by-pass line 11 by-passes the reformer 9 to provide unreformed hydrocarbon fuel into the fuel inlet 13 of the high temperature fuel cell stack 3 to control the temperature of the stack 3.

[0016] In a third embodiment, the hydrocarbon fuel reformer 9 is located separately from but thermally integrated with the high temperature fuel cell stack 3. A start-up burner 15 is thermally integrated with the reformer 9. Preferably but not necessarily, a start-up burner 15 effluent outlet conduit 17 is fluidly connected to an oxidizer inlet 19 of the high temperature fuel cell stack 3. This configuration allows the system 1 to be started up using only the hydrocarbon fuel and oxidizer without oxidizing SOFC anode electrodes. This configuration eliminates a separately stored reducing or inert purge gas that is flushed through the system to prevent the anode electrodes of the SOFCs from oxidizing.

[0017] In a fourth embodiment, a carbon monoxide separation device 21, such as pressure swing adsorption (PSA) device is fluidly connected to a fuel exhaust (i.e., the fuel outlet) 23 of the stack 3. A carbon monoxide recycle conduit 25 has an inlet that is connected to the outlet of the carbon monoxide separation device 21 and an outlet that is fluidly connected to a fuel inlet 13 of the high temperature fuel cell stack 3. For example, the device 21 allows carbon monoxide to be separately recirculated into a hydrocarbon fuel inlet conduit 27 of the stack 3 to enhance the electrochemical reaction in the fuel cells of the stack 3. Furthermore, since carbon monoxide is recirculated, less carbon monoxide is provided into the atmosphere than if the carbon monoxide from the system was simply flared or vented into the atmosphere.

[0018] In a fifth preferred embodiment, a PSA hydrogen separation device 29 is fluidly connected to the fuel exhaust 23 of the stack 3. A thermal output of the high temperature fuel stack 3 in addition to the fuel exhaust is thermally integrated with at least a first column of the PSA device 29 to heat

the first column. This use of the stack 3 waste heat to heat a PSA column under purge allows a reduction in the compression requirements of the PSA device and/or an increase in the amount of gas purification for the same level of compression.

[0019] In a sixth preferred embodiment, a solid oxide fuel cell system with an improved balance of plant efficiency comprises a thermally integrated reformer, combustor and stack, where the reformer is heated by the stack cathode exhaust, by radiative and convective heat from the stack and by the combustor heat during steady state operation. In a seventh preferred embodiment, the system starts up with hydrogen generated using a CPDX (catalytic partial oxidation) reactor. In an eighth preferred embodiment, the system contains an energy efficient and self sufficient water management subsystem. The system contains at least one evaporator which uses stack anode exhaust to heat water being provided into the inlet fuel stream.

I. First Embodiment

[0020] The elements of the system 1 of the first embodiment will now be described. In prior art systems, organosulfur compounds (e.g., mercaptans, thiophenes) contained in natural gas fuel are hydrogenated by adding hydrogen to the fuel inlet stream and reacting the mixture in a desulfurizer over a suitable catalyst, such as cobalt-molybdenum. The reaction produces CH_4 and H_2S gases. The H_2S gas is subsequently removed by reaction with a fixed sorbent bed, containing for example ZnO or other suitable materials for removing this gas. Usually these reactions are carried out at about 300°C ., and the catalyst and sorbent can be contained in the same vessel.

[0021] FIG. 1 illustrates an embodiment of a desulfurizer subsystem of the first embodiment, which comprises the desulfurizer 5 and the water-gas shift reactor 7 that are thermally integrated with each other.

[0022] The desulfurizer 5 preferably comprises the catalyst, such as Co—Mo or other suitable catalysts, which produces CH_4 and H_2S gases from hydrogenated, sulfur containing natural gas fuel, and a sorbent bed, such as ZnO or other suitable materials, for removing the H_2S gas from the fuel inlet stream. Thus, a sulfur free or reduced sulfur hydrocarbon fuel, such as methane or natural gas leaves the desulfurizer 5.

[0023] The water-gas shift reactor 7 may be any suitable device which converts at least a portion of the water exiting the fuel cell stack 3 fuel exhaust 23 into free hydrogen. For example, the reactor 7 may comprise a tube or conduit containing a catalyst which converts some or all of the carbon monoxide and water vapor in the tail gas exiting exhaust 23 through a fuel exhaust conduit 31 into carbon dioxide and hydrogen. The catalyst may be any suitable catalyst, such as an iron oxide or a chromium promoted iron oxide catalyst. The reactor 7 is preferably located along conduit 31 between the fuel exhaust 23 and the PSA hydrogen separation device 29. The reactor 7 works in tandem with the PSA hydrogen separation device 29 by increasing the amount of free hydrogen in the fuel side exhaust (i.e., anode exhaust or tail gas) by converting some water present in the fuel side exhaust gas into hydrogen. The reactor 7 then provides hydrogen and carbon dioxide to the PSA hydrogen separation device 29, which separates the hydrogen from the carbon dioxide. Thus, some of the water present in the fuel may be converted to hydrogen in the reactor 7.

[0024] The desulfurizer 5 and the water-gas shift reactor 7 are thermally integrated with each other. This means that

waste heat from the reactor 7 is transferred directly or indirectly to the desulfurizer 5. For example, the desulfurizer 5 and the water-gas shift reactor 7 may be located in the same hot box such that they are thermally integrated with each other. Alternatively, the desulfurizer 5 and the water-gas shift reactor 7 may be located in thermal contact with each other (i.e., in direct physical contact or by contacting the same thermal mass). Alternatively, the desulfurizer 5 and the water-gas shift reactor 7 may be connected by a thermal conduit, such as a pipe containing a thermal transfer fluid, such as water/steam or another fluid.

[0025] The desulfurizer 5 is fluidly connected to the fuel inlet 13 of the fuel cell stack 3. The water-gas shift reactor 7 is fluidly connected to the fuel exhaust 23 of the fuel cell stack. The term fluidly connected means that the connection may be direct or indirect, as long as a gas or liquid fluid may be provided through the connection. Preferably, the desulfurizer 5 is connected to the fuel inlet 13 of the fuel cell stack 3 by the fuel inlet conduit 27. A valve 28 controls the flow of fuel through conduit 27. The water-gas shift reactor 7 is connected to the fuel exhaust 23 of the fuel cell stack 3 by the fuel exhaust conduit 31. It should be noted that the conduits 27 and 31 shown in FIG. 1 contain several portions or sections that are separated by various processing devices, such as the desulfurizer 5 and the water-gas shift reactor 7.

[0026] A method of operating the fuel cell system 1 according to the first embodiment includes providing a hydrocarbon fuel, such as natural gas, into a desulfurizer 5 from a hydrocarbon fuel source 33, such as a natural gas supply pipe or a hydrocarbon fuel storage tank or vessel. The fuel is desulfurized in the desulfurizer 5 and is then provided directly or indirectly into the fuel cell stack 3 through conduit 27 and inlet 13, as will be described in more details with respect to the other embodiments of the present invention.

[0027] The warm fuel exhaust is provided from the fuel cell stack 3 through exhaust 23 and conduit 31 into the water-gas shift reactor 7. Preferably, the exhaust has given up some of the heat in heat exchangers and other devices prior to entering the reactor. For example, an optional fuel heat exchanger and water vaporizer 35 may be provided between the conduits 27 and 31. The vaporizer 35 humidifies the fuel inlet stream in conduit 27. The vaporizer 35 can be a device which supplies water vapor based on cyclic desiccant beds or a rotating desiccant wheel (i.e., “enthalpy wheel”) and which provides water vapor from an exhaust stream in conduit 31 into the fuel inlet stream in conduit 27 or the vaporizer 35 can be a steam generator which provides water vapor into the fuel inlet stream from another water source.

[0028] The warm exhaust gases react with each other according to the forward water gas shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, in the reactor 7 and give up or provide heat to the desulfurizer 5 side and the incoming fuel gases passing through it. Preferably, the reactor 7 supplies all of the heat that is needed to operate the desulfurizer 5 at its standard operating temperature, such as at least about 300°C ., and no other heating means or heaters are used to heat the desulfurizer 5.

[0029] The hydrogen, carbon monoxide, carbon dioxide and water vapor containing exhaust continues in conduit 31 to an optional condenser 37, optional water knockout or separation device 39 and a compressor 41, such as a reciprocating compressor, to the PSA hydrogen 29 and/or carbon monoxide 21 separation devices. The water knock out system 39 separates the water from the fuel exhaust stream and discharges it

out of the water discharge conduit **43** controlled by valve **45**, or recirculates it into the fuel heat exchanger and water vaporizer **35** using a positive displacement pump **47**. The water is preferably provided into the stack **3** when the stack **3** is operated to generate hydrogen while generating little or no electricity in the fuel cell mode (i.e., no net electricity is produced in the fuel cell mode), as will be described in more detail below. The additional water is used to support fuel reforming as needed. An optional water inlet conduit **49** may also be connected to the water knockout device **39**. Additional water may be provided for bootstrapping, as the electrochemical process will ordinarily generate net water. A flow control valve **51** position is controlled mechanically or by a computer dependent on the water level in the water knockout device. The valve **51** controls the amount of water provided into device **39** through conduit **49** based on the water level in the device **39**.

II. Second Embodiment

[0030] FIG. 1 illustrates a system **1** of the second embodiment containing the hydrocarbon fuel by-pass line **11** which allows feeding the fuel cell stack **3** with an accurately controlled fuel input mixture for improved control of broad range of operating conditions, such as stack **3** operating temperature.

[0031] In the prior art, SOFCs are commonly operated with hydrocarbon fuels, such as methane. The methane may be partially or fully steam reformed to form hydrogen and carbon oxides before it enters the SOFC stack. Steam reformation is an endothermic process. If methane is only partially steam reformed, the remaining methane will be reformed within the SOFC. The endothermic reaction within the SOFC stack affects the thermal balance of the SOFC stack.

[0032] Oxidation of hydrocarbons in the high temperature fuel cells includes an endothermic reaction in which the hydrocarbon fuel, such as methane or natural gas, is converted to hydrogen and carbon oxides. This endothermic reaction may not be obvious in the net reaction occurring in the fuel cell system. One example is a solid oxide fuel cell fed with methane. In the net reaction, the methane is oxidized to carbon dioxide and water. However, it is electrochemically highly unlikely for the methane to be directly oxidized to the products. It is commonly assumed that some methane first reacts with steam, which is almost always present, to form hydrogen and carbon oxides. Then the hydrogen and lower carbon oxides are oxidized. The water formed by the oxidation of hydrogen can enable steam reformation of yet unconverted methane. The result of this intermediate chemical reaction is heat consumption at the location of the steam reformation.

[0033] Heat consumed by reformation inside the fuel cell thereby creates a cooling effect. This cooling effect can be localized and create temperature gradients and in turn thermal stresses which can damage part of the fuel cell. Thus, the reformation is partly or completely performed outside the fuel cell stack.

[0034] In the system **1** of the second embodiment, the hydrocarbon fuel reformer **9** is located separately from the high temperature fuel cell stack **3**. The reformer is adapted to at least partially reform a hydrocarbon fuel into a hydrogen fuel. The hydrocarbon fuel is provided into the reformer **9** through the hydrocarbon fuel inlet conduit **27**, connected to

an inlet of the reformer **9**. A connecting conduit **53** connects the fuel inlet **13** of the high temperature fuel cell stack **3** with an outlet of the reformer **9**.

[0035] The hydrocarbon fuel reformer **9** may be any suitable device which is capable of partially or wholly reforming a hydrocarbon fuel to form a carbon containing and free hydrogen containing fuel. For example, the fuel reformer **9** may be any suitable device which can reform a hydrocarbon gas into a gas mixture of free hydrogen and a carbon containing gas. For example, the fuel reformer **9** may reform a humidified biogas, such as natural gas, to form free hydrogen, carbon monoxide, carbon dioxide, water vapor and optionally a residual amount of unreformed biogas. The free hydrogen and carbon monoxide are then provided into the fuel inlet **13** of the fuel cell stack **3** through conduit **53**.

[0036] In a preferred aspect of the second embodiment, the fuel reformer **9** is thermally integrated with the fuel cell stack **3** to support the endothermic reaction in the reformer **9** and to cool the stack **3**. The term “thermally integrated” in this context means that the heat from the reaction in the fuel cell stack **3** drives the net endothermic fuel reformation in the fuel reformer **9**. The fuel reformer **9** may be thermally integrated with the fuel cell stack **3** by placing the reformer **9** and stack **3** in the same hot box and/or in thermal contact with each other, or by providing a thermal conduit or thermally conductive material which connects the stack **3** to the reformer **9**. While less preferred, a separate heater may also be used to heat the reformer **9** instead of or in addition to the heat provided from the stack **3**.

[0037] The hydrocarbon fuel by-pass line **11** is fluidly connected to the fuel inlet **13** of the high temperature fuel cell stack **3**. In other words, the by-pass line may be connected directly to the inlet **13** or it may be indirectly connected to the inlet **13** via the connecting conduit **53**. The terms “line” and “conduit” are used interchangeably, and include gas flow pipes and other fluid flow ducts. The by-pass line **11** is adapted to provide unreformed hydrocarbon fuel into the fuel inlet **13** of the high temperature fuel cell stack **3**.

[0038] Preferably, the by-pass line **11** branches off from the hydrocarbon fuel inlet conduit **27** upstream of the reformer **9** and connects to the connecting conduit **53** downstream of the reformer **9**. Preferably, the desulfurizer **5** is located upstream of a location where the by-pass line **11** branches off from the hydrocarbon fuel inlet conduit **27**, such that sulfur is removed from the unreformed hydrocarbon fuel provided through the by-pass line **11**.

[0039] Alternatively, the by-pass line **11** does not have to branch off from the fuel inlet conduit **27**. In this case, the by-pass line **11** is connected to a separate source of hydrocarbon fuel, such as a natural gas pipe or a storage vessel. In this case, a separate desulfurizer is provided in the by-pass line **11**.

[0040] The system **1** further comprises a hydrocarbon fuel flow control valve **55** in the by-pass line **11**. The control valve **55** is adapted to control a flow of the unreformed hydrocarbon fuel into the fuel cell stack to control a temperature and/or other operating parameters of the fuel cell stack. The valve **55** may be manually or remotely controlled by an operator. Alternatively, the valve **55** may be automatically controlled by a computer or other processing device. The valve **55** may be controlled automatically or by an operator in response to detected or predetermined parameters. For example, the temperature or other parameters of the fuel cell stack **3** may be detected by a temperature detector or other detectors, and the results provided to an operator or a computer. The operator or

computer then adjust the valve **55** to control the flow of the unreformed hydrocarbon fuel through the by-pass line **11** into the fuel cell stack **3** to control the fuel cell stack temperature or other parameters. Alternatively, the by-pass valve **55** may be adjusted based on predetermined parameters, such as based on time of stack **3** operation that is stored in the computer memory.

[0041] A method of operating a high temperature fuel cell system **1** of the second embodiment includes providing a hydrocarbon fuel into a reformer **9** through the fuel inlet conduit **27** and at least partially reforming the hydrocarbon fuel into hydrogen fuel in the reformer **9**. The hydrogen fuel from the reformer **9** is provided into a fuel inlet of a high temperature fuel cell stack **3** through conduit **53**. The unreformed hydrocarbon fuel that does not pass through the reformer **9** is provided into the fuel inlet of the high temperature fuel cell stack **3** through the by-pass line **11** and optionally through conduit **53**. The flow of the unreformed hydrocarbon fuel through the by-pass line **11** that does not pass through the reformer **9** is controlled by the valve **55** to control a temperature and/or other operating parameters of the high temperature fuel cell stack **3**.

[0042] The oxidation of hydrogen or low carbon oxides inside a fuel cell is an exothermic reaction. Heat generated by the exothermic oxidation should be removed to attain stable operation. Unreformed methane can aid in the removal of heat via the above described steam reformation in the reformer **9**.

[0043] Accurately controlling the amount of unreformed hydrocarbons entering the stack allows control of the temperature of the fuel cells in the stack. In an external reformer, the degree of reformation depends on a variety of factors some of which may vary during operation. Thus, a simple way of controlling the amount of unreformed hydrocarbons entering the stack is the by-pass line **11** which by-passes the external reformer **9** as shown in FIG. 1. The bypass valve **55** controls the amount of unreformed hydrocarbons entering the stack **3**. More specifically, the least amount of hydrocarbons entering the stack **3** is limited by the finite conversion inside the external reformer. An upper limit for the amount of unreformed hydrocarbons entering the stack **3** is posed by reformation occurring outside the external reformer along by-pass line **11**.

[0044] This method of the second embodiment is applicable not only to solid oxide fuel cells, but any high temperature fuel cell fed by a fuel which undergoes reformation reactions prior to oxidation. In the example provided above, the reformation is an endothermic reaction, but there are also reformation reactions that are exothermic. Examples of exothermic reformation include but are not limited to partial oxidation of methane. Methane, which is the major constituent of natural gas, is a very common example of a hydrocarbon fuel that undergoes reformation, but other hydrocarbon fuels, such as natural gas, propane and butane are possible. Therefore the reformer by-pass **11** is applicable to various reformation reactions and a variety of hydrocarbon fuels.

[0045] FIG. 2 illustrates a system **101** of the first and second embodiments having an alternative configuration from the system **1** shown in FIG. 1. In the system **101** shown in FIG. 2, the fuel heat exchanger and water vaporizer **35** is located upstream of the desulfurizer **5**. Thus, the fuel enters the heat exchanger and water vaporizer **35** prior to entering the desulfurizer. The desulfurizer **5** and the water-gas shift reactor **7** are located in the same hot box **103** (i.e., a warm box or fuel conditioner). The fuel conditioner **103** also contains the cata-

lytic start-up burner **15**, the fuel heat exchanger and water vaporizer **35** and an optional fuel pre-reformer **105** which is thermally integrated with a fuel exhaust heat exchanger **107**. Thus, the catalytic start-up burner **15** in the system **101** is located in the fuel conditioner **103** rather than thermally integrated with the fuel cell stack **3**. The start-up burner **15** is fed by the stack fuel exhaust conduit **31** rather than by the hydrocarbon fuel inlet conduit **27**.

[0046] The fuel cell stack **3** is thermally integrated with the reformer **9** in the same hot box **108**. The hot box **108** also contains an optional radiative air heater **109** and an optional catalytic tail gas burner **110**. The tail gas burner **110** is provided with hydrocarbon fuel from a branch **111** of the hydrocarbon fuel inlet conduit **27**, which is regulated by valve **112**. A valve **113** directs the fuel exhaust flow between the PSA hydrogen separation device **29** and the tail gas burner **110**. The oxidizer side components are the same as in system **1** and will be described in more detail below.

III. Third Embodiment

[0047] FIG. 1 illustrates a system **1** of the third embodiment, where the system is brought up from room temperature to operating conditions (i.e., at start-up) with only hydrocarbon fuel and air. No stored nitrogen or hydrogen are required to protect the anodes from oxidation. The stack **3**, reformer **9** and start-up burner **15** comprise separate devices which are thermally integrated with each other, such as being located in the same hot box and/or being in thermal contact with each other and/or being connected by a thermal fluid transfer conduit.

[0048] The anodes of SOFC systems are commonly made from materials including metal oxides which have to be reduced to attain electron conductivity and thereby enable the electrochemical reaction in the anode chamber. Metallic oxides used include, but are not limited to nickel oxide. One common difficulty with these metallic oxides is the necessity to keep them reduced once they have been reduced. Re-oxidation causes significant if not catastrophic performance degradation. The prevention of re-oxidation is a technical challenge for the start-up of a SOFC system.

[0049] Commonly, the fuel cell anode chamber is flushed with inert or reducing gases, such as nitrogen or hydrogen, at start-up to prevent anode electrode re-oxidation. For systems operated on hydrocarbon fuels, nitrogen or hydrogen are not readily available. Instead one or both gases are stored separately within or near the system for consumption during start-up.

[0050] The inventor has realized that a SOFC system can be built and operated such that the anode can be maintained in its reduced state while the system is operating only on hydrocarbon fuel and air during start-up. FIG. 1 illustrates one configuration of a SOFC system **1** according to the third embodiment.

[0051] As shown in FIG. 1, the start-up burner **15** is thermally integrated with the reformer **9** and the reformer **9** is thermally integrated with the stack **3**. As discussed above, the term "thermally integrated" includes location in the same hot box, located in thermal contact with each other and/or connection by a thermal transfer fluid conduit. The hydrocarbon fuel inlet conduit **27** is fluidly connected to an inlet of the reformer **9** and to a first inlet of the start-up burner **15** (such as via the burner fuel delivery conduit **73**). A burner oxidizer inlet conduit **57** is connected to a second inlet of the start-up burner **15**. The start-up burner **15** effluent outlet conduit **17** is

fluidly connected to an oxidizer inlet **19** of the high temperature fuel cell stack **3**. For example, the effluent outlet conduit **17** may be connected directly into the oxidizer inlet **19** of the stack or it may be connected to an oxidizer inlet conduit **59** which is connected to the oxidizer inlet **19** of the stack **3**. The system also contains an oxidizer blower **61**, such as an air blower, which provides the oxidizer into the burner and stack through the conduits **57** and **59**, and an oxidizer exhaust conduit **63** which removes oxidizer exhaust from the stack **3**. The system also contains an optional air filter **65** and an optional heat exchanger **67** which heats the oxidizer being provided into the stack **3** through the oxidizer inlet conduit **59** using the heat of the oxidizer exhaust being provided through the oxidizer exhaust conduit **63**. The system also contains valves **69** and **71** in conduits **57** and **59**, respectively. The system also contains a burner fuel delivery conduit **73** which is regulated by valve **75**. The conduit **73** branches off from conduit **27** or it may comprise a separate fuel delivery conduit.

[0052] The method of operating the system **1** according to the third embodiment is as follows. Initially all components of the system are at room temperature. The anodes of the SOFC stack are reduced from previous operation. Valves **69** and **75** in conduits **57** and **73**, respectively, are open, while valve **71** in conduit **59** is closed.

[0053] Hydrocarbon fuel, which can be natural gas, and an oxidizer, such as air or oxygen, are injected into the start-up burner **15** through conduits **73** and **57**, respectfully. The fuel and oxidizer are ignited in the burner **15** by an ignitor. The heat stream from the combustion in the burner **15** is directed at the thermally integrated reformer **9**. The effluent of the burner **15** is directed through conduits **17** and **59** into the oxidizer inlet **19** (i.e., cathode chamber(s)) of the stack **3**. The effluent is exhausted from the stack **3** through conduit **63** and from there into the air heat exchanger **67**. It may be advantageous to operate the burner lean on fuel to ensure that the cathode chamber(s) of the fuel cells in the stack are always exposed to an oxidizing environment. The combustion raises primarily the temperature of the reformer **9**, secondarily the stack **3** temperature, and finally the air heat exchanger **67** temperature.

[0054] Fuel is directed through the desulfurizer **5**, vaporizer **35** and the reformer **9**, into the stack **3** fuel inlet **13** (i.e., into the anode chamber(s) of the fuel cells in the stack). The fuel may be directed into inlet **13** simultaneously with injecting fuel and oxidizer into the burner **15**. Alternatively, the fuel may be directed into the inlet **13** after it is directed into the burner **15** but before the stack **3** reaches the anode oxidation temperature. The fuel exhaust exits the stack **3** through conduit **31** and water-gas shift reactor **7**. The fuel picks up heat in the reformer **9** and in the stack **3** and transports the heat to the water gas shift reactor **7** which is thermally coupled to the desulfurizer **5**. Thereby the desulfurizer **5** is heated to operating conditions by the stack **3** exhaust, as provided in the first embodiment. Some heat is also delivered to the water vaporizer **7**.

[0055] The heat balance in the system is designed such that the reformer **9** reaches its operating temperature (i.e., the temperature at which it reforms the hydrocarbon fuel) before the stack **3** anode chamber(s) reaches a temperature where re-oxidation of the anode electrodes could occur. Also, enough heat is carried to the water vaporizer **35** such that the

inflowing fuel is sufficiently humidified to avoid carbon formation in the hot components downstream of the water vaporizer **35**.

[0056] If these method parameters are satisfied, the SOFC anode electrodes will be exposed to a hydrogen rich feed stream created by steam reformation in the reformer **9** when a temperature at the anode is reached at which re-oxidation can occur. At the same time, the desulfurizer **5** is brought to operating temperature early enough to avoid detrimental effects of excessive sulfur content in the fuel feed stream. One preferred hydrocarbon fuel for this system is natural gas. However other fuels, including but not limited to methane, propane, butane, or even vaporized liquid hydrocarbons can be utilized.

[0057] After the start-up of the system **1** is completed (i.e., once the stack reaches desired steady state operating conditions), hydrocarbon fuel and oxidizer supply into the start-up burner is terminated either by an operator or automatically by a computer and the start-up burner is turned off. Valves **69** and **75** are closed and valve **71** is opened to provide an oxidizer into the oxidizer inlet **19** of the solid oxide fuel cell stack **3**. The stack **3** then operates in the fuel cell mode to generate electricity from an electrochemical reaction of the fuel provided through conduit **27** and reformer **9** (and optionally through by-pass line **11**) and oxidizer provided through conduit **59**. Thus, it should be noted that the oxidizer is preferably not provided into oxidizer inlet **19** of the solid oxide fuel cell stack **3** while the start-up burner **15** operates. Furthermore, no separately stored reducing or inert gases are used to flush the anode chambers of the solid oxide fuel cells of the stack **3** during the start-up.

IV. Fourth Embodiment

[0058] FIG. **1** illustrates a system **1** of the fourth embodiment, where the carbon monoxide and hydrogen are separately extracted from the fuel exhaust stream and recirculated into the fuel inlet stream and/or removed from the system for other use.

[0059] The system **1** contains a hydrogen separation or purification device **29** fluidly connected to a fuel exhaust **23** of the stack **3**. Preferably, the device **29** comprises a PSA device that is connected to the exhaust **23** of the stack **3** by the fuel exhaust conduit **31**. The PSA device **29** is adapted to separate at least a portion of hydrogen from the fuel exhaust while the fuel cell stack **3** generates electricity in a fuel cell mode. A reciprocating pump **41** provides the fuel exhaust into the PSA device **29**. The hydrogen separation or purification device **29** preferably contains the carbon monoxide separation device or unit **21** and a carbon dioxide/water separation device or unit **30**. Preferably, the devices **21** and **30** comprise PSA devices which respectively separate carbon monoxide and carbon dioxide/water from the fuel exhaust and allow hydrogen to pass through. Preferably, but not necessarily, the PSA device **21** is located in series with and downstream from PSA device **30**. However, if desired, the PSA device **21** may be located upstream of PSA device **30**. Preferably, PSA devices **21** and **30** comprise different units of a single PSA system **29**, where each unit **21** and **30** contains at least two PSA columns.

[0060] A carbon monoxide recycle conduit **25** recirculates the carbon monoxide from the PSA device **21** into the fuel inlet conduit **27**. A carbon dioxide/water removal conduit **26** removes carbon dioxide and water from device **30**. The inlet of conduit **25** is connected to the outlet of the carbon monox-

side separation device **21** and the outlet of conduit **25** is fluidly connected to the fuel inlet of the high temperature fuel cell stack **3**, such as via the fuel inlet conduit **27**. Alternatively, the outlet of the carbon monoxide recycle conduit **25** may be connected directly into the reformer **9** and/or into the fuel inlet **13** of the stack **3**.

[0061] The system further comprises an optional hydrogen recycle conduit **77** which is controlled by a recirculated hydrogen flow control valve **79**. The inlet of the conduit **77** is connected to the outlet of the hydrogen separation device **29**. The outlet of the conduit **77** is fluidly connected to the fuel inlet **13** of the high temperature fuel cell stack **3**, such as directly connected to the inlet **13** or indirectly connected via the fuel inlet conduit **27**. If desired, the conduit **77** may be omitted and hydrogen and carbon monoxide may be carried together through conduit **25**, which may result in a higher purity product or lower compression requirements. If desired, the flow of hydrogen passed through conduit **25** may be metered.

[0062] Preferably, the outlet of conduits **25** and **77** are merged together into a recycle conduit **81**, which provides the recirculated hydrogen and carbon monoxide into the fuel inlet conduit **27**, as shown in FIG. 1, or directly into the reformer **9** and/or the stack **3** fuel inlet **13**. However, the recycle conduit **81** may be omitted, and the conduits **25** and **77** may separately provide carbon monoxide and hydrogen, respectively, into conduit **27**, reformer **9** and/or stack **3** fuel inlet **13**. The system **1** also optionally contains a hydrogen removal conduit **83**, which removes hydrogen from the system **1** for storage or for use in a hydrogen using device, as will be described in more detail below.

[0063] FIG. 3 illustrates an exemplary two column PSA hydrogen separation device **29**, such as, for example, the carbon dioxide/water separation unit **30** of a larger device or system **29** which also contains the carbon monoxide separation unit **21** shown in FIG. 1. Preferably, the PSA device **29** operates on a Skarstrom-like PSA cycle. The classic Skarstrom cycle consists of four basic steps: pressurization, feed, blowdown, and purge. The device **29** contains two columns **83** and **85**. When one column is undergoing pressurization and feed, the other column is undergoing blowdown and purge. In one exemplary configuration, the device **29** may be operated using three three-way valves **87**, **89** and **91** and one or more flow restrictors **93**. Of course other configurations may also be used. When the three-way valves are in the positions shown in FIG. 3, the pressurization and feed steps are essentially combined, and the blowdown and purge steps are similarly combined.

[0064] The PSA device **29** operates as follows. A pressurized feed gas (F), such as the fuel exhaust gas, containing CO₂, H₂O, CO and H₂ is provided through the fuel exhaust conduit **31**. Two-position, three-way valves **87**, **89** and **91** are simultaneously switched to the state shown in FIG. 3A. The feed is introduced to column **83** via valve **87** pressurizing column **83**. The adsorbent contained in column **83** selectively adsorbs the CO₂ and H₂O. As the feed continues to flow, most of the H₂ exits as extract (E) via valve **91**. The extract may be provided into conduits **77** and/or **83** shown in FIG. 1, or into the carbon monoxide PSA device **21** to remove carbon monoxide from the extract. The device **21** operates in the same way as the portion of the device **29** shown in FIG. 3, except the bed materials in the columns are selected to separate hydrogen from carbon monoxide.

[0065] The switching of valve **89** exposes column **85** to a low pressure line, resulting in the blowdown of column **85**. The low pressure line **95** is the output of column **83** that passes through one or more flow restrictors **93**. Gases that were previously adsorbed during the previous cycle desorb and flow out through valve **89**, producing a desorbate stream (D). The desorbate stream may be provided into the carbon monoxide PSA device **21** to remove carbon monoxide from the desorbate stream. Meanwhile, a relatively small quantity of high pressure extract gas flows through the flow restrictor(s) **93** and through column **85** in the direction opposite to the feed flow, forming a purge flow that helps remove desorbate from column **85**.

[0066] At a subsequent time, as column **83** approaches saturation, the positions of all valves are switched. Thus, column **85** becomes the column fed via valve **87** and is pressurized, and column **83** vents via valve **89** and blows down. In this way the purity of the extract gas E is maintained.

[0067] A method of operating the system **1** of the fourth embodiment will now be described. A fuel and an oxidizer are provided into the fuel cell stack **3** through conduits **27/53** and **59**, respectively. A fuel side exhaust stream is generated from the fuel cell stack **3** through conduit **31** while the fuel and the oxidizer are provided into the fuel cell stack **3** operating in a fuel cell mode (i.e., while the stack is generating electricity). At least a portion of the hydrogen is separated from the fuel side exhaust stream by the PSA hydrogen separation device **29** during the fuel cell mode operation. For example, the hydrogen and carbon monoxide are separated from carbon dioxide and water in the PSA carbon dioxide/water separation device or unit **30**. Then, at least a portion of carbon monoxide is separated from the fuel side exhaust stream (i.e., from the hydrogen) in the PSA carbon monoxide separation device or unit **21**. At least a portion of the separated carbon monoxide is recirculated from PSA device **21** through conduits **25** and **81** into the fuel inlet gas stream in the fuel inlet conduit **27** and/or in conduit **53**. The separated hydrogen from the PSA device **29** may also be recirculated into the fuel inlet gas stream through conduits **77** and **81**, or provided to a hydrogen storage vessel or to a hydrogen using device **115** outside the system **1** through conduit **83**, or both. The valve **79** may be used to determine the portion of the separated hydrogen being provided through conduits **77** and **83**.

V. Fifth Embodiment

[0068] FIGS. 1 and 4 illustrate a system **1** of the fifth embodiment, which utilizes hydrogen separation from the fuel exhaust stream using temperature-assisted pressure swing adsorption. In this system, the fuel cell stack **3** thermal output and the PSA hydrogen separation device **29** are thermally integrated. In FIG. 4, the carbon dioxide/water separation unit **30** of the device **29** is illustrated for clarity.

[0069] A high temperature fuel cell system **1**, such as a SOFC system, produces hydrogen by way of hydrocarbon reforming reactions that occur within the stack **3** and/or within the reformer **9**. The hydrogen appears in the system's tailgas (i.e., the stack exhaust), and can be effectively separated and purified in a pressure-swing adsorption (PSA) device **29**. The gas compression costs associated with the PSA process can be considerable. The process of the fifth embodiment takes advantage of heat available from the other parts of the system **1** to reduce those compression costs.

[0070] The PSA device **29** operates with a pressure differential between its pressurization/loading and blow-down/

purge steps. The pressure differential, and the associated change in loading of the adsorbed gases, produces the gas separation. Generally, the higher the pressure differential, the more effective the separation and the less amount of purge gas required. As shown in the example of FIG. 3, the product gas is typically used as the purge gas, and so its use often needs to be minimized. Typically, the pressure ratio of the pressurization to purge steps is approximately 10:1, and approximately 10 to 20% of the product gas is lost as purge.

[0071] The SOFC stack 3 often operates at pressures near ambient, and thus the fuel exhaust or tailgas containing hydrogen is also near ambient. In a typical non-thermally integrated design, in order to reach pressures effective for PSA, the tailgas should be compressed by about a factor of 10. This pressurization is usually not an issue for hydrogen production plants that use steam methane reforming, because they often operate at about 10 atmospheres pressure or above.

[0072] If heat is provided during purging steps and removed during loading steps, the separation process can be made more effective. This would allow a lower level of compression to be used to achieve a similar separation objective. Alternatively, a higher degree of purification may be achieved for the same level of compression. This can occur because the loading of a adsorbed gas is a strong function of temperature as well as pressure.

[0073] In many separation systems it is not cost-effective to produce and remove this heat. In a high temperature fuel cell system, such as a SOFC system, however, heat of an adequate quality is readily available.

[0074] In one example shown in FIG. 4, warm exhaust air from the stack 3 flowing through oxidizer exhaust conduit 63 is used to heat a PSA column under purge 85, and cool inlet air flowing through the oxidizer inlet conduit 59 is used to cool a column 83 under load.

[0075] In another example, a coolant fluid may circulate between the stack 3 operating at an elevated temperature and the PSA separation system 29 through a circulation conduit. The fluid removes excess heat from the stack 3 and carries it to the separation system 29, where it is used to heat the gas used to purge the columns. There are a wide variety of ways to achieve these effects using the various heat sources available in a high temperature fuel cell system, such as a SOFC system.

[0076] Thus, in the system of the fifth embodiment, the compression requirements for a pressure-swing adsorption separation system for hydrogen are reduced by using waste heat from a SOFC stack to effect a more efficient separation. Alternatively, a higher degree of purification may be achieved for the same level of compression. In other words, the extract purity is improved if the column being purged could be heated with heat originating from a high temperature fuel cell stack, and the column being fed could be cooled. Alternatively, the pressure of the feed gas might be reduced, or the amount of purge gas might be reduced, while the extract purity was maintained. The benefits of this method are reduced capital equipment costs associated with compression and/or higher product value associated with higher purity.

[0077] While the method of fifth embodiment was described with respect to the carbon dioxide/water separation unit 30 of the PSA hydrogen separation device 29, it may also be used with the PSA carbon dioxide separation device or unit 21 in addition to or instead of the carbon dioxide/water separation unit 30. In this case, the waste heat from the high temperature fuel cell system is used to heat the column under

purge in the carbon monoxide separation device 21 in addition to or instead of the column under purge in the carbon dioxide/water separation unit 30. This may be accomplished by providing heat from the oxidizer exhaust conduit 63 to the column under purge in device 21 and/or by providing heat from the coolant fluid in the circulation conduit. If desired, the column under load in the device 21 may be cooled by the cool inlet air flowing through the oxidizer inlet conduit 59.

[0078] Since each column of the PSA devices 21 and 29 is alternated between being the column under load and column under purge, the oxidizer inlet conduit 59 and the oxidizer exhaust conduit 63 are thermally integrated with all columns of each applicable PSA device 21 and/or 29, as shown in FIG. 5. For example, each conduit 59, 63 may be split into as many parallel branches as there are columns in the respective PSA device. Each branch 59A, 59B, 63A, 63B of the respective conduit 59, 63 is thermally integrated with a respective column 83, 85, of the PSA 29 device. The flow of cool or hot air through each branch is controlled by a valve 88. In other words, each PSA device column 83 and 85 is thermally integrated with a branch 59A, 63A and 59B, 63B of both conduits 59 and 63. However, only cool or warm air is provided to a particular column depending on if the column is undergoing loading or purging.

[0079] Likewise, if the coolant fluid is circulated between the stack 3 operating at an elevated temperature and the PSA separation system 29 through a circulation conduit, then the circulation conduit is split into parallel branches, and each branch is thermally integrated with a respective PSA column. The flow of the coolant fluid is controlled to each branch by a valve, such that the warm coolant fluid flows only to those columns that are undergoing purging.

[0080] It should be noted that the term “thermally integrated” in the context of the fifth embodiment means that the conduit either thermally contacts the respective PSA column or that it is located adjacent to and preferably in the same thermal enclosure, such as a hot box or thermal insulation, as the respective PSA column, to be able to transfer heat to the column.

[0081] FIG. 6 illustrates an alternative example of a PSA unit 21 or 30 of the PSA device 29, where all gas flows are decoupled. In the PSA system shown in FIG. 6, if valves V1, V2 and V3 (numbered 87, 89 and 91 in FIG. 3) are replaced by pairs of two-way valves V1A-V3B (i.e., a two-way valve would be placed on each horizontal branch stemming from valves V1-V3, and locations V1, V2 and V3 corresponding to the valves 87, 89 and 91 become “T” shaped conduit junctions), flow restrictors 93 are replaced by actuating valves V4A and V4B, and the extract line is valved (V5), then all flows can be decoupled. In particular, the blowdown/purge steps can be decoupled and the pressurization/feed steps can be decoupled. This may have advantages in terms of improvement of purity and reduction of purge losses, although at the cost of additional equipment. Furthermore, the lengths of the feed and purge steps can be decoupled. Either can be of arbitrary length. Clearly this can interrupt the flow of purified extract, and so occasionally additional beds are provided that increase the system’s flexibility and do not interrupt the flow.

VI. Sixth Embodiment

[0082] The elements of a system 201 of the sixth embodiment will now be described with respect to FIG. 7. Elements in FIG. 7 with the same numbers as in FIGS. 1 and 2 should be presumed to be the same unless noted otherwise. If desired,

the system **201** may be used with any one or more suitable elements of the first, second, third, fourth and/or fifth embodiments, even if these elements are not explicitly shown in FIG. 7.

[0083] In the sixth embodiment, steam methane reformation (SMR) is used to preprocess natural gas before it is fed into the stack **3** for co-generation of hydrogen and electricity from natural gas or other hydrocarbon fuel using a solid oxide fuel cell system (i.e., a regenerative or a non-regenerative system). SMR transforms methane to reaction products comprising primarily carbon monoxide and hydrogen, as described above. These reaction products are then oxidized in the SOFC stack **3** at high temperature producing electricity. Excess hydrogen is retrieved as a side product. Steam methane reformation reactions are endothermic reactions which require heat, while oxidation reactions in SOFC stack **3** are exothermic reactions which generate heat. This provides a synergy for tight heat integration to improve overall Balance of Plant (BOP) energy efficiency. By integration of reformer **9** and stack **3** in the hot box **108**, heat from the stack **3** can be transferred to the reformer **9** using convective, radiative and/or conductive heat transfer.

[0084] In system **1** illustrated in FIG. 1, the reformer **9** is thermally integrated with the stack **3** for heat transfer from the stack **3** to the reformer **9**. The stack **3** generates enough heat to conduct the SMR reaction in the reformer **9** during steady-state operation of the system **1**. However, under some different operating conditions ranging from low to high stack efficiency and fuel utilization, the exothermic heat generated by the stack **3** and provided to the reformer **9** may be in greater than, the same as or less than the heat required to support the steam methane reforming reaction in the reformer **9**. The heat generated and/or provided by the stack **3** may be less than required to support steam reformation in the reformer **9** due to low fuel utilization, high stack efficiency, heat loss and/or stack failure/turndown. In this case, supplemental heat is supplied to the reformer **9**.

[0085] In a preferred aspect of the sixth embodiment, the system **201** provides the supplemental heat to the reformer **9** to carry out the SMR reaction during steady state operation. The supplemental heat may be provided from a burner **15** (more generally referred to in this embodiment as a combustor) which is thermally integrated with the reformer **9** and/or from a cathode (i.e., air) exhaust conduit which is thermally integrated with the reformer **9**. While less preferred, the supplemental heat may also be provided from the anode (i.e., fuel) exhaust conduit which is thermally integrated with the reformer. Preferably, the supplemental heat is provided from both the combustor **15** which is operating during steady state operation of the reformer (and not just during start-up) and from the cathode (i.e., air) exhaust of the stack **3**. Most preferably, the combustor **15** is in direct contact with the reformer **9**, and the stack cathode exhaust conduit **203** is configured such that the cathode exhaust contacts the reformer **9** and/or wraps around the reformer **9** to facilitate additional heat transfer. This lowers the combustion heat requirement for SMR.

[0086] Preferably, the reformer **9** is sandwiched between the combustor **15** and one or more stacks **3** to assist heat transfer, as illustrated in FIGS. 8-10 and as described in more detail below. The combustor **15**, when attached to the reformer **9**, closes the heat balance and provides additional heat required by the reformer. When no heat is required by the reformer, the combustor unit acts as a heat exchanger. Thus, the same combustor (i.e., burner) **15** may be used in both

start-up and steady-state operation of the system **201**. When using combustion catalysts coated on the conduit walls, natural gas is preferably introduced at several places in the combustion zone to avoid auto ignition and local heating.

[0087] Preferably, one or more sensors are located in the system **201** which are used to determine if the reformer requires additional heat and/or how much additional heat is required. These sensors may be reformer temperature sensor (s) which measure the reformer temperature and/or process parameter sensor(s), which measure one or more of fuel utilization, stack efficiency, heat loss and stack failure/turn-down. The output of the sensor(s) is provided to a computer or other processor and/or is displayed to an operator to determine if and/or how much additional heat is required by the reformer. The processor or operator then controls the combustor heat output based on the step of determining to provide an desired amount heat from the combustor to the reformer. The combustor heat output may be controlled by controlling the amount of fuel and air being provided into the combustor or by shutting off the fuel and/or air being provided into the combustor. The combustor may be controlled automatically by the processor or manually by operator actions.

[0088] Preferably, the combustor **15** exhaust is provided into the inlet of the air heat exchanger **67** through conduit **205** to heat the air being provided into the stack **3** through the exchanger **67**. Thus, the stack cathode exhaust is provided to the exchanger **67** indirectly through the combustor **15**. The configuration of system **201** differs from that of system **1** illustrated in FIG. 1 where the stack cathode exhaust is provided directly into the exchanger **67** through conduit **63**.

[0089] The reformer **9** is located in close proximity to the stack **3** to provide radiative and convective heat transfer from the stack **3** to the reformer. Preferably, the cathode exhaust conduit **203** of the stack **3** is in direct contact with the reformer **9** and one or more walls of the reformer **9** may comprise a wall of the stack cathode exhaust conduit **203**. Thus, the cathode exhaust provides convective heat transfer from the stack **3** to the reformer **9**.

[0090] Furthermore, if desired, the cathode exhaust from the stack may be wrapped around the reformer **9** by proper ducting and fed to the combustion zone of the combustor **15** adjacent to the reformer **9** before exchanging heat with the incoming air in the external air heat exchanger **67**, as shown in FIGS. 8-10 and as described in more detail below. Natural gas or other hydrocarbon fuel can be injected and mixed with cathode exhaust air in the combustion zone of the combustor **15** to produce heat as needed.

[0091] FIGS. 8-10 illustrate three exemplary configurations of the stack, reformer and combustor unit in the hot box **108**. However, other suitable configurations are possible. The reformer **9** and combustor **15** preferably comprise vessels, such as fluid conduits, that contain suitable catalysts for SMR reaction and combustion, respectively. The reformer **9** and combustor **15** may have gas conduits packed with catalysts and/or the catalysts may be coated on the walls of the reformer **9** and/or the combustor **15**.

[0092] The reformer **9** and combustor **15** unit can be of cylindrical type, as shown in FIG. 8A or plate type as shown in FIGS. 9A and 10A. The plate type unit provides more surface area for heat transfer while the cylindrical type unit is cheaper to manufacture.

[0093] Preferably, the reformer **9** and combustor **15** are integrated into the same enclosure and more preferably share at least one wall, as shown in FIGS. 8-10. Preferably, but not

necessarily, the reformer **9** and combustor **15** are thermally integrated with the stack(s) **3**, and may be located in the same enclosure, but comprise separate vessels from the stack(s) **3** (i.e., external reformer configuration).

[0094] In a preferred configuration of the system **201**, fins **209** are provided in the stack cathode exhaust conduit **203** and in the burner **15** combustion zone **207** to assist with convective heat transfer to the reformer **9**. In case where the reformer **9** shares one or more walls with the cathode exhaust conduit **203** and/or with the combustion zone **207** of the burner **15**, then the fins are provided on the external surfaces of the wall(s) of the reformer. In other words, in this case, the reformer **9** is provided with exterior fins **209** to assist convective heat transfer to the interior of the reformer **9**.

[0095] FIGS. **8A** and **8B** show the cross-sectional top and front views, respectively, of an assembly containing two stacks **3** and a cylindrical reformer **9** combustor **15** unit **210**. The combustion zone **207** of the combustor **15** is located in the core of the cylindrical reformer **9**. In other words, the combustor **15** comprises a catalyst containing channel bounded by the inner wall **211** of the reformer **9**. In this configuration, the combustion zone **207** is also the channel for the cathode exhaust gas. The space **215** between the stacks **3** and the outer wall **213** of the reformer **9** comprises the upper portion of the stack cathode exhaust conduit **203**. Thus, the reformer inner wall **211** is the outer wall of the combustor **15** and the reformer outer wall **213** is the inner wall of the upper portion of stack cathode exhaust conduit **203**. If desired, a cathode exhaust opening **217** can be located in the enclosure **219** to connect the upper portion **215** of conduit **203** with the lower portions of the conduit **203**. The enclosure **219** may comprise any suitable container and preferably comprises a thermally insulating material.

[0096] In operation, a natural gas (and/or other hydrocarbon fuel) and steam mixture is fed to the lower end of the reformer **9** through conduit **27**. The reformed product is provided from the reformer **9** into the stack anode (fuel) inlet **13** through conduit **53**. The spent fuel is exhausted from the stack through the anode exhaust **23** and conduit **31**.

[0097] The air enters the stack through the cathode (air) inlet **19** and exits through exhaust opening **217**. The system **201** is preferably configured such that the cathode exhaust (i.e., hot air) exists on the same side of the system as the inlet of the reformer **9**. For example, as shown in FIG. **8B**, since the mass flow of hot cathode exhaust is the maximum at the lower end of the device, it supplies the maximum heat where it is needed, at feed point of the reformer **9** (i.e., the lower portion of the reformer shown in FIG. **8B**). In other words, the mass flow of the hot air exiting the stack is maximum adjacent to the lower portion of the reformer **9** where the most heat is needed. However, the cathode exhaust and reformer inlet may be provided in other locations in the system **201**. The hot air containing cathode exhaust is preferably but not necessarily, provided into the combustion zone **207** of the combustor **15** through conduit **203**.

[0098] Natural gas is also injected into the central combustion zone **207** of the combustor **15** where it mixes with the hot cathode exhaust. The circular or spiral fins are preferably attached to the inner **211** and outer **213** reformer walls to assist heat transfer. Heat is transferred to the outer wall **213** of the reformer **9** from the stack **3** by convection and radiation. Heat is transferred to the inner wall **211** of the reformer by convection and/or conduction from the combustion zone **207**.

As noted above, the reformer and combustion catalysts can either be coated on the walls or packed in respective flow channels.

[0099] FIGS. **9A** and **9B** show the cross-sectional top and front views, respectively, of an assembly containing two stacks **3** and a plate type reformer **9** coupled with a plate type combustor **15**. The configuration of the plate type reformer-combustor unit **220** is the same as the cylindrical reformer-combustor unit **210** shown in FIGS. **8A** and **8B**, except that the reformer-combustor unit **220** is sandwich shaped between the stacks. In other words, the combustion zone **207** is a channel having a rectangular cross sectional shape which is located between two reformer **9** portions. The reformer **9** portions comprise channels having a rectangular cross sectional shape. The fins **209** are preferably located on inner **211** and outer **213** walls of the reformer **9** portions. The plate type reformer and combustion unit **220** provides more surface area for heat transfer compared to the cylindrical unit **210** and also provides a larger cross-sectional area for the exhaust gas to pass through.

[0100] FIGS. **10A** and **10B** show the cross-sectional top and front views, respectively, of an assembly containing one stack **3** and a plate type reformer **9** coupled with a plate type combustor **15**. Exhaust gas is wrapped around the reformer **9** from one side. One side of the combustion zone **207** channel faces insulation **219** while the other side faces the reformer **9** inner wall **213**.

VII. Seventh Embodiment

[0101] Hot box **108** components, such as the stack **3** and reformer **9** are heated to a high temperature before starting (i.e., during the start-up mode) to draw current from the stack as well as produce hydrogen. Furthermore, the stack is preferably run in a reducing environment or ambient using hydrogen until the stack heats up to a reasonably high temperature below the steady state operating temperature to avoid reoxidation of the anode electrodes. Stored hydrogen can be used for this process. However, in the seventh preferred embodiment, a small CPDX (catalytic partial oxidation) unit is used in the start-up mode of the system, to make the system independent of external source of hydrogen.

[0102] FIG. **7** illustrates the system **201** containing the CPDX unit **223**. Any suitable CPDX device may be used. However, it should be noted that the CPDX unit may be used during start-up of other suitable SOFC systems, such as systems **1** and **101** shown in FIGS. **1** and **2**, respectively.

[0103] The system **201** preferably also includes a start-up heater **225** for heating the CPDX unit **223** during start-up and a mixer **227** for mixing air and a hydrocarbon fuel, such as methane or methane containing natural gas. The air and fuel are provided into the mixer through conduits **229** and **231**, respectively. The mixed air and fuel are provided into the CPDX unit **223** after being mixed in the mixer **227**.

[0104] The CPDX unit **223** produces hydrogen from the air and fuel mix. The produced hydrogen is sent with excess oxygen and nitrogen through conduit **233** to the reformer **9**. The hydrogen passes through the reformer **9**, the stack **3**, the fuel heat exchanger **35**, the shift reactor **7** and the condenser unit **37** and is provided to the combustor **15** through conduit **235**. The hydrogen is burned in the combustor **15** to heat up the reformer **9** and stack **15**. This process is continued until the system heats up to a certain temperature, such as a temperature at which oxidation of the anode electrodes is avoided. Then the CPDX unit **223** is stopped or turned off,

and a hydrocarbon fuel, such as natural gas, is injected directly into the combustor **15** through conduit **73** to continue the heating process. The combustor **15** is thermally integrated with the reformer **9** and can be used during the start-up and during steady state operation modes.

VIII. Eighth Embodiment

[0105] FIG. 7 illustrates the system **201** with components configured for efficient water management. However, it should be noted that the below described components may also be configured for efficient water management for other suitable SOFC systems, such as systems **1** and **101** shown in FIGS. 1 and 2, respectively.

[0106] A SOFC system in general can be self sufficient in water. Heat is required to make steam required for the methane reformation. Water from anode exhaust may be condensed and recycled back to the system. Furthermore, water and natural gas may be fed to a heat exchanger for transferring heat from the anode exhaust. However, under some operating conditions, the heat recovered from anode exhaust gas may not be sufficient to evaporate all the water needed in the reformation reaction as well as to heat the fuel inlet steam mixture to a desired temperature before feeding this mixture to the reformer. Thus, additional water heating and management components may be added to the system **201** to evaporate all the water needed in the reformation reaction as well as to heat the fuel inlet steam mixture to a desired temperature before feeding this mixture to the reformer.

[0107] The system **201** shown in FIG. 7 contains an additional evaporator **237**, an optional supplemental heater/evaporator **239** and a steam/fuel mixer **241**. The system operates as follows. The process of steam generation, mixing steam with fuel, such as natural gas, and preheating mixture may be done in four steps.

[0108] First, metered water is provided from the condenser **37** through condensate pump **243**, water knockout/tank **39**, metering pump **47** and optional water treatment device **245** into the evaporator **237**. The metered water is heated and at least partially evaporated in the evaporator **237** by the heat from the anode exhaust provided into evaporator from the shift reactor **7** through conduit **31**.

[0109] Second, the partially evaporated water is provided from evaporator **237** into the supplemental heater/evaporator **239**. Supplemental heat is supplied in the heater/evaporator **239** to complete the evaporation process and superheat the steam.

[0110] Third, the steam is provided from the heater/evaporator **239** into the steam/fuel mixer **241**. The steam is mixed with the fuel in the mixer.

[0111] Fourth, the fuel and steam mix is provided from the mixer **241** into the fuel heat exchanger **35**, where the mix is preheated using heat from the hot anode exhaust. The fuel and steam mix is then provided into the reformer through conduit **27**.

[0112] Water vapor transfer devices such as enthalpy wheels can be added to the system to reduce the heat required for the total evaporation process. These devices can transfer water vapor from the anode exhaust to incoming fuel stream.

[0113] As described above, the anode exhaust provided into the condenser **37** is separated into water and hydrogen. The hydrogen is provided from the condenser **37** via conduit **247** into the conduit **31** leading to the hydrogen purification subsystem **29** and into conduit **235** leading into the combustor **15**. The flow of hydrogen from condenser **37** through conduits

31 and **235** may be controlled by one three way valve or by separate valves **249** and **251** located in conduits **31** and **235**, respectively. The hydrogen from the hydrogen purification system **29** may be provided to the use/storage subsystem **115** via conduit **83**, while the carbon monoxide from subsystem **29** is provided to the burner or combustor **15** and carbon monoxide and water from subsystem **29** are exhausted.

IX. Electricity and Hydrogen Generation

[0114] The electrochemical (i.e., high temperature fuel cell) system of the preferred embodiments of the present invention such as the solid oxide electrochemical system, such as a SOFC or a SORFC system, or the molten carbonate fuel cell system, can be used to co-produce hydrogen and electricity in the fuel cell mode. Thus, while the prior art SORFC system can generate either electricity in the fuel cell mode or hydrogen in an electrolysis mode, the system of the preferred embodiments of the present invention can co-produce both hydrogen and electricity (i.e., produce hydrogen and electricity together). The system of the preferred embodiments generates a hydrogen rich exhaust stream using reforming reactions that occur within the fuel cell stack and/or in a reformer in thermal integration with the fuel cell stack. The amount of hydrogen produced can be controlled by the operator. The hydrogen rich stream is further conditioned if necessary and stored or used directly by the operator. Thus, the high temperature electrochemical systems produce purified hydrogen as a by-product of fuel reformation in the fuel cell mode. The electrochemical system may operate in the fuel cell mode, when no external electricity input is required, to generate diffusion of ions across an electrolyte of the system. In contrast, a reversible or regenerative electrochemical system operates in the electrolysis mode when external electricity is required to generate diffusion of ions across the electrolyte of the system.

[0115] It should be noted that the electrochemical system of the preferred embodiments does not necessarily co-produce or co-generate power or electricity for use outside the system. The system may be operated to primarily internally reform a carbon and hydrogen containing fuel into hydrogen with minimal power generation or without delivering or outputting power from the system at all. If desired, a small amount of power may be generated and used internally within the system, such as to keep the system at operating temperature and to power system components in addition to other parasitic loads in the system.

[0116] Thus, in one aspect of the preferred embodiments of the present invention, the high temperature electrochemical system is a SOFC or a SORFC system which co-produces electricity and hydrogen in the fuel cell mode. A SOFC or SORFC system operates in the fuel cell mode when oxygen ions diffuse through an electrolyte of the fuel cells from the oxidizer side to the fuel side of the fuel cell containing the carbon and hydrogen containing gas stream. Thus, when the high temperature electrochemical system, such as a SOFC or SORFC system operates in the fuel cell mode to generate hydrogen, a separate electrolyzer unit operating in electrolysis mode and which is operatively connected to the fuel cell stack is not required for generation of hydrogen. Instead, the hydrogen is separated directly from the fuel cell stack fuel side exhaust gas stream without using additional electricity to operate a separate electrolyzer unit.

[0117] When an SORFC system is used rather than an SOFC system, the SORFC system can be connected to a

primary source of electricity (e.g., grid power) and can accept electricity from the primary source when desirable or can deliver electricity to the primary source when desirable. Thus, when operating the SORFC system of the preferred embodiments, the system operator does not have to sacrifice electricity production to produce hydrogen and vice versa. The SORFC system does not require a hot thermal mass which absorbs heat in the fuel cell mode and which releases heat in the electrolysis mode for operation or energy storage. However, a hot thermal mass may be used if desired. Furthermore, the system may use, but does not require a fuel reformer.

[0118] Furthermore, a relative amount of hydrogen and electricity produced can be freely controlled. All or a portion of the hydrogen in the fuel side exhaust stream may be recirculated into the fuel inlet stream to provide control of the amount of electricity and hydrogen being co-produced in the system, as will be described in more detail below. The hydrogen product can be further conditioned, if necessary, and stored or used directly in a variety of applications, such as transportation, power generation, cooling, hydrogenation reactions, or semiconductor manufacture, either in a pressurized or a near ambient state.

[0119] The system **1** or **101** shown in FIGS. **1** and **2** derives power from the oxidation of a carbon and hydrogen containing fuel, such as a hydrocarbon fuel, such as methane, natural gas which contains methane with hydrogen and other gases, propane or other biogas, or a mixture of a carbon fuel, such as carbon monoxide, oxygenated carbon containing gas, such as methanol, or other carbon containing gas with a hydrogen containing gas, such as water vapor, H₂ gas or their mixtures. For example, the mixture may comprise syngas derived from coal or natural gas reformation. Free hydrogen is carried in several of the system process flow streams. The carbon containing fuel is provided into the system from a fuel source, which may comprise a fuel inlet into the fuel cell stack, a fuel supply conduit and/or a fuel storage vessel.

[0120] The fuel cell stack **3** preferably contains the fuel cells, separator plates, seals, gas conduits, heaters, thermal insulation, control electronics and various other suitable elements used in fuel cell stacks.

[0121] The system **1**, **101** and **201** also contains at least one hydrogen separator, such as the PSA hydrogen separation device **29**. The system **1**, **101** and **201** also contains an optional hydrogen conditioner **114**, as shown in FIGS. **1** and **2**. The hydrogen conditioner **114** may be any suitable device which can purify, dry, compress (i.e., a compressor), or otherwise change the state point of the hydrogen-rich gas stream provided from the hydrogen separator **29**. If desired, the hydrogen conditioner **114** may be omitted.

[0122] The system **1**, **101** and **201** also contains a hydrogen storage/use subsystem **115**, as shown in FIG. **2**. This subsystem **115** may comprise a hydrogen storage vessel, such as a hydrogen storage tank, a hydrogen dispenser, such as a conduit which provides hydrogen or a hydrogen-rich stream to a device which uses hydrogen, or a hydrogen using device. For example, the subsystem **115** may comprise a conduit leading to a hydrogen using device or the hydrogen using device itself, used in transportation, power generation, cooling, hydrogenation reactions, or semiconductor manufacture.

[0123] For example, the system **1**, **101** and **201** may be located in a chemical or a semiconductor plant to provide primary or secondary (i.e., backup) power for the plant as well as hydrogen for use in hydrogenation (i.e., passivation of

semiconductor device) or other chemical reactions which require hydrogen that are carried out in the plant.

[0124] Alternatively, the subsystem **115** may also comprise another fuel cell, such as an SOFC or SORFC or any other fuel cell, which uses hydrogen as a fuel. Thus, the hydrogen from the system **1**, **101** and **201** is provided as fuel to one or more additional fuel cells **115**. For example, the system **1**, **101** and **201** may be located in a stationary location, such as a building or an area outside or below a building and is used to provide power to the building. The additional fuel cells **115** may be located in vehicles located in a garage or a parking area adjacent to the stationary location. In this case, the carbon and hydrogen containing fuel is provided to the system **1**, **101** and **201** to generate electricity for the building and to generate hydrogen which is provided as fuel to the fuel cell **115** powered vehicles. The generated hydrogen may be stored temporarily in a storage vessel and then provided from the storage vessel to the vehicle fuel cells **115** on demand (analogous to a gas station) or the generated hydrogen may be provided directly from the system **1**, **101** and **201** to the vehicle fuel cells **115**.

[0125] In one preferred aspect of the present invention, the hydrogen separator **29** is used to separate and route hydrogen from the fuel side exhaust stream only into the subsystem **115**. In another preferred aspect of the present invention, the hydrogen separator **29** is used to separate hydrogen from the fuel side exhaust stream and to route all or a part of the hydrogen back into the fuel inlet **13** of the fuel cell stack **3** through conduit **81**, to route all or part of the hydrogen to the subsystem **115** and/or to route the hydrogen out with the tail gas.

[0126] A preferred method of operating the systems **1**, **101** and **201** will now be described. The systems are preferably operated so that excess fuel is provided to the fuel cell stack **3**. Any suitable carbon containing and hydrogen containing fuel is provided into the fuel cell stack. The fuel may comprise a fuel such as a hydrocarbon fuel, such as methane, natural gas which contains methane with hydrogen and other gases, propane or other biogas. Preferably, an unreformed hydrocarbon fuel from the by-pass valve **11** and a hydrogen fuel from the reformer **9** are provided into the stack **3**.

[0127] Alternatively, the fuel may comprise a mixture of a non-hydrocarbon carbon containing gas, such as carbon monoxide, carbon dioxide, oxygenated carbon containing gas such as methanol or other carbon containing gas with a hydrogen containing gas, such a water vapor or hydrogen gas, for example the mixture may comprise syngas derived from coal or natural gas reformation. The hydrogen and water vapor may be recycled from the fuel side exhaust gas stream or provided from hydrogen and water vapor conduits or storage vessels.

[0128] The reformation reactions occur within the fuel cell stack **3** and/or in the reformer **9** and result in the formation of free hydrogen in the fuel side exhaust gas stream. For example, if a hydrocarbon gas such as methane is used as a fuel, then the methane is reformed to form a mixture containing non-utilized hydrogen, carbon dioxide and water vapor in the fuel cell stack **3**. If natural gas is used as a fuel, then the natural gas may be converted to methane in a preprocessing subsystem or it may be reformed directly to a non-hydrocarbon carbon containing gas such as carbon monoxide in the reformer **9**.

[0129] Preferably, the fraction of hydrogen separated by the hydrogen separator **29** and the amount of total fuel provided

to the fuel cell stack **3** for electricity and hydrogen production are variable and under the control of an operator operating a control unit of the system. An operator may be a human operator who controls the hydrogen separation and electricity production or a computer which automatically adjusts the amount of hydrogen separation and electricity production based on predetermined criteria, such as time, and/or based on received outside data or request, such as a demand for electricity by the power grid and/or a demand for hydrogen by the subsystem **115**. Controlling these two parameters allows the operator to specify largely independently the amount of hydrogen produced and the amount of electricity generated. The outside data or request may comprise one or more of electricity demand, hydrogen demand, electricity price and hydrogen price, which may be transmitted electronically to a computer system operator or visually or audibly to a human system operator.

[0130] In one extreme, when the user of the system needs electricity, but does not need additional hydrogen, then the operator can choose to have the hydrogen containing streams recirculated back into the fuel cell stack **3** by the separator **29** through conduit **81** by opening valve **79**, while providing no hydrogen or a minimum amount of hydrogen to the subsystem **115**, through conduit **83**, where hydrogen flow may also be controlled by a valve.

[0131] In another extreme, when the user of the system needs hydrogen, but does not need any electricity generated, the operator can choose to have the fuel cell stack **3** act primarily to internally reform the carbon containing fuel into hydrogen with minimal power generation and/or minimal or no external power output/delivery from the system. A small amount of power may be generated to keep the system at operating temperature and to power the hydrogen separator **29** and conditioner **114**, if necessary, in addition to other parasitic loads in the system. All or most of the hydrogen from the separator **29** is provided to the subsystem **115** rather than to the conduit **81**. In this case, additional water from the water supply **39** is preferably added to the fuel.

[0132] In the continuum between the two extremes, varying amounts of hydrogen and electricity may be needed simultaneously. In this case, the operator can choose to divert varying amounts of the hydrogen from the separator **29** to conduits **81** and **83**, while simultaneously generating the desired amount of electricity. For example, if more hydrogen is recirculated back into the fuel cell stack **3** through conduit **81** by controlling valve **79**, then more electricity is generated but less hydrogen is available for use or storage in the subsystem **115**. The trade off between the amount of electricity and hydrogen produced can vary based on the demand and the price of each.

[0133] The trade off between the amount of electricity and hydrogen generated may also be achieved using several other methods. In one method, the amount of fuel provided to the fuel cell stack **3** is kept constant, but the amount of current drawn from the stack **3** is varied. If the amount of current drawn is decreased, then the amount of hydrogen provided to the hydrogen separator **29** is increased, and vice versa. When less current is drawn, less oxygen diffuses through the electrolyte of the fuel cell. Since the reactions which produce free hydrogen (i.e., the steam-methane reforming reaction (if methane is used as a fuel) and the water-gas shift reaction) are substantially independent of the electrochemical reaction, the decreased amount of diffused oxygen generally does not substantially decrease the amount of free hydrogen provided in the fuel side exhaust gas stream.

[0134] In an alternative method, the amount of current drawn from the stack is kept constant, but the amount of fuel provided to the stack **3** is varied. If the amount of fuel provided to the stack **3** is increased, then the amount of hydrogen provided to the hydrogen separator **29** is increased, and vice versa. The amount of fuel may be varied by controlling the flow of fuel through the fuel inlet conduit **27** by a computer or operator controlled valve **28** and/or by controlling the flow of fuel through the by-pass line **11** by valve **55**.

[0135] In another alternative method, both the amount of current drawn and the amount of fuel provided into the fuel cell stack **3** are varied. The amount of hydrogen generated generally increases with decreasing amounts of drawn current and with increasing amounts of fuel provided into the fuel cell stack. The amount of hydrogen generated generally decreases with increasing amounts of drawn current and with decreasing amounts of fuel provided into the fuel cell stack.

[0136] Preferably, the systems of the preferred embodiments may be operated at any suitable fuel utilization rate. Thus, 0 to 100 percent of the fuel may be utilized for electricity production. Preferably, 50 to 80 percent of the fuel is utilized for electricity production and at least 10 percent, such as 20 to 50 percent, of the fuel is utilized for hydrogen production. For example, a 100 kWe SOFC system may be used to generate from about 70 to about 110 kWe of electricity and from about 45 to about 110 kg/day of high pressure hydrogen when 50 to 80 percent of the fuel is utilized for electricity production. The systems of the preferred embodiments may be used to produce hydrogen cost effectively. Thus, the method of the preferred embodiments provides a reduction in the cost of hydrogen production.

[0137] If the fuel cell stack **3** is a solid oxide regenerative fuel cell (SORFC) stack which is connected to a primary source of power (such as a power grid) and a source of oxidized fuel (such as water, with or without carbon dioxide), then the device can operate transiently in an electrolysis mode as an electrolyzer to generate hydrogen streams, methane streams, or mixtures when economically advantageous (e.g., when the cost of electricity is inexpensive compared to the cost of the fuel containing bound hydrogen), or during times when the demand for hydrogen significantly exceeds the demand for electricity. At other times, the system **1**, **101** and **201** can be used in the fuel cell mode to generate electricity from the stored hydrogen or carbon containing fuel. Thus, the system **1**, **101** and **201** can be used for peak shaving.

[0138] The fuel cell systems described herein may have other embodiments and configurations, as desired. Other components, such as fuel side exhaust stream condensers, heat exchangers, heat-driven heat pumps, turbines, additional gas separation devices, hydrogen separators which separate hydrogen from the fuel exhaust and provide hydrogen for external use, fuel preprocessing subsystems, fuel reformers and/or water-gas shift reactors, may be added if desired, as described, for example, in U.S. application Ser. No. 10/300,021, filed on Nov. 20, 2002, in U.S. Provisional Application Ser. No. 60/461,190, filed on Apr. 9 2003, and in U.S. application Ser. No. 10/446,704, filed on May 29, 2003 all incorporated herein by reference in their entirety. Furthermore, it should be understood that any system element or method step described in any embodiment and/or illustrated in any figure herein may also be used in systems and/or methods of other suitable embodiments described above, even if such use is not expressly described.

[0139] The foregoing description of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The description was chosen in order to explain the principles of the invention and its practical application. It is intended that the scope of the invention be defined by the claims appended hereto, and their equivalents.

What is claimed is:

1. A method of operating a solid oxide fuel cell system, comprising:

operating the fuel cell system in a start-up mode by:

- providing a hydrocarbon fuel and air into a catalytic partial oxidation reactor;
- generating hydrogen in the catalytic partial oxidation reactor;
- providing the generated hydrogen into a solid oxide fuel cell stack; and

stopping the generation of hydrogen in the catalytic partial oxidation reactor once the fuel cell stack reaches a predetermined operating temperature; and

operating the fuel cell system in a steady state operating mode to generate electricity after the fuel cell stack reaches a predetermined operating temperature.

2. The method of claim 1, wherein the predetermined operating temperature is a temperature at which oxidation of anode electrodes of solid oxide fuel cells in the solid oxide fuel cell stack is avoided.

3. The method of claim 1, further comprising heating the catalytic partial oxidation reactor during the start-up mode.

4. The method of claim 1, further comprising mixing the hydrocarbon fuel and air and providing the mixed hydrocarbon fuel and air into the catalytic partial oxidation reactor.

5. The method of claim 1, wherein the hydrocarbon fuel comprises methane or methane containing natural gas.

6. The method of claim 1, wherein the generated hydrogen is provided in the start-up mode from the catalytic partial oxidation reactor into the solid oxide fuel cell stack through a reformer.

7. The method of claim 6, wherein the generated hydrogen is provided in the start-up mode from the solid oxide fuel cell stack into a fuel heat exchanger.

8. The method of claim 7, wherein the generated hydrogen is provided in the start-up mode from the fuel heat exchanger into a combustor.

9. The method of claim 1, wherein the step of stopping the generation of hydrogen in the catalytic partial oxidation reactor comprises stopping operation of the catalytic partial oxidation reactor.

10. The method of claim 1, wherein operating the fuel cell system in a steady state operating mode comprises:

- providing the hydrocarbon fuel and water vapor into a reformer;
- reforming the hydrocarbon fuel in the reformer to form a hydrogen containing reaction product; and

providing the reaction product and air into the solid oxide fuel cell stack during the steady state operating mode of the stack.

11. The method of claim 10, wherein operating the fuel cell system in a steady state operating mode further comprises: providing the hydrocarbon fuel into a fuel heat exchanger; providing the hydrocarbon fuel from the fuel exchanger into the reformer; providing the air into an air heat exchanger; and providing the air from the air heat exchanger into the solid oxide fuel cell stack.

12. The method of claim 11, wherein operating the fuel cell system in a steady state operating mode further comprises: providing an anode exhaust from the solid oxide fuel cell stack into the fuel heat exchanger to heat the hydrocarbon fuel; providing at least a portion of the anode exhaust from the fuel heat exchanger into a combustor; providing a cathode exhaust from the solid oxide fuel cell stack into the combustor; and providing a combustor exhaust into the air heat exchanger to heat the air.

13. The method of claim 1, wherein operating the fuel cell system in a start-up mode further comprises: providing the generated hydrogen from the catalytic partial oxidation reactor a reformer; providing the generated hydrogen from the reformer into the solid oxide fuel cell stack; providing the generated hydrogen from the solid oxide fuel cell stack into a fuel heat exchanger; and providing the generated hydrogen from the fuel heat exchanger into a combustor.

14. The method of claim 13, wherein operating the fuel cell system in a steady state operating mode comprises: providing the hydrocarbon fuel into a fuel heat exchanger; providing the hydrocarbon fuel from the fuel exchanger into the reformer; providing water vapor into the reformer; reforming the hydrocarbon fuel in the reformer to form a hydrogen containing reaction product; providing the reaction product into the solid oxide fuel cell stack; providing the air into an air heat exchanger; providing the air from the air heat exchanger into the solid oxide fuel cell stack; providing an anode exhaust from the solid oxide fuel cell stack into the fuel heat exchanger to heat the hydrocarbon fuel; providing at least a portion of the anode exhaust from the fuel heat exchanger into a combustor; providing a cathode exhaust from the solid oxide fuel cell stack into the combustor; and providing a combustor exhaust into the air heat exchanger to heat the air.

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