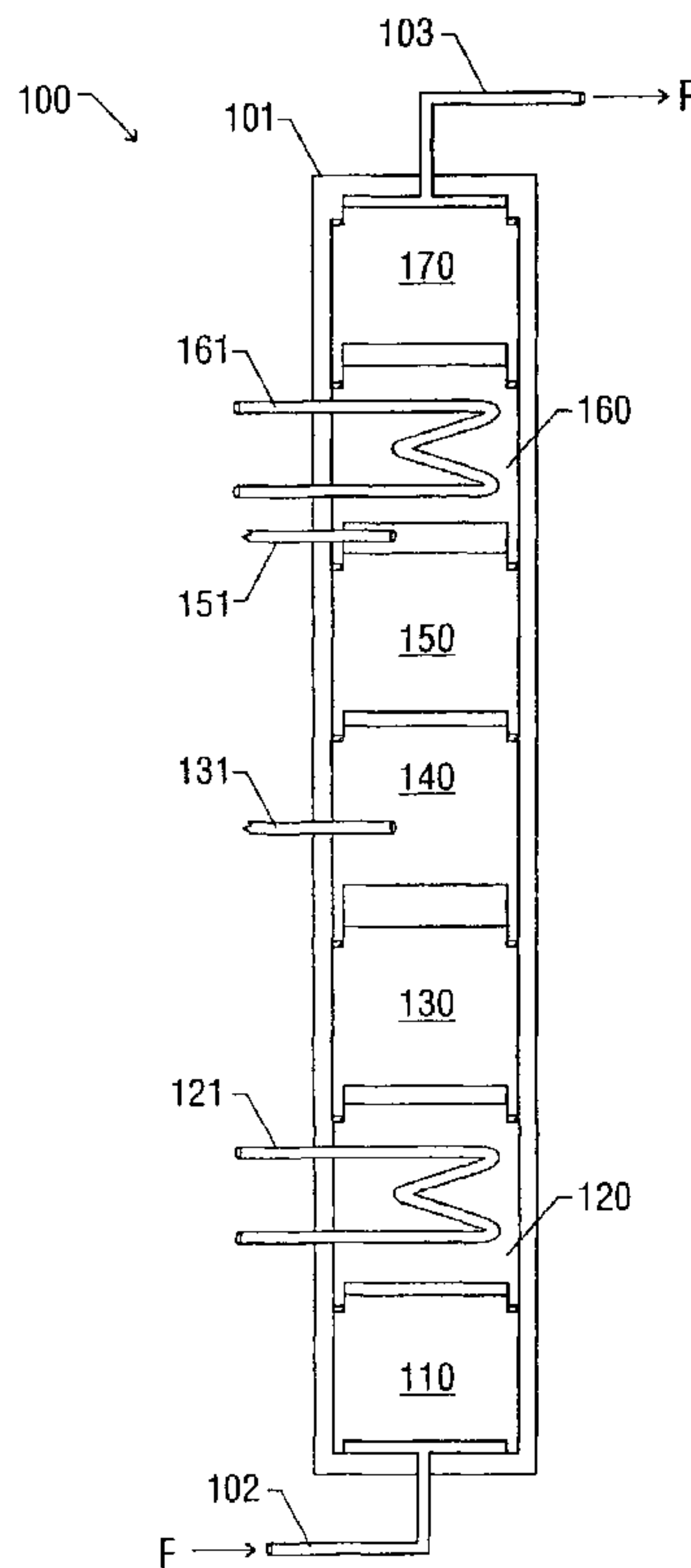




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(54) Titre : PROCESSEUR DE COMBUSTIBLE COMPACT POUR PRODUCTION DE GAZ RICHE EN HYDROGENE
 (54) Title: COMPACT FUEL PROCESSOR FOR PRODUCING A HYDROGEN RICH GAS



(57) **Abrégé/Abstract:**

An apparatus (100) including a plurality of modules stacked end-to-end along a common axis and a multi-step process of converting hydrocarbon fuel (F) to a substantially pure hydrogen gas (P) using said apparatus (100). Each module includes a shell having an interior space defining a passeway for the flow of gas from a first end of the shell to a second end of the shell opposite the first end, and a processing core being contained within the interior space for effecting a chemical, thermal, or physical change to a gas stream passing axially through the module. In one embodiment, said plurality of modules including a first module (110) containing a partial oxidation catalyst and steam reforming catalyst, a second module (120) containing a first

(57) **Abrégé(suite)/Abstract(continued):**

heat exchanger (121), a third module (130) containing a desulfurization agent, a fourth module (140) containing an inert material for mixing components of gas stream passing there through, a fifth module (150) containing a water gas shift catalyst bed, a sixth module (160) containing a second heat exchanger (161) and a seventh module (170) containing a carbon monoxide oxidation catalyst bed.

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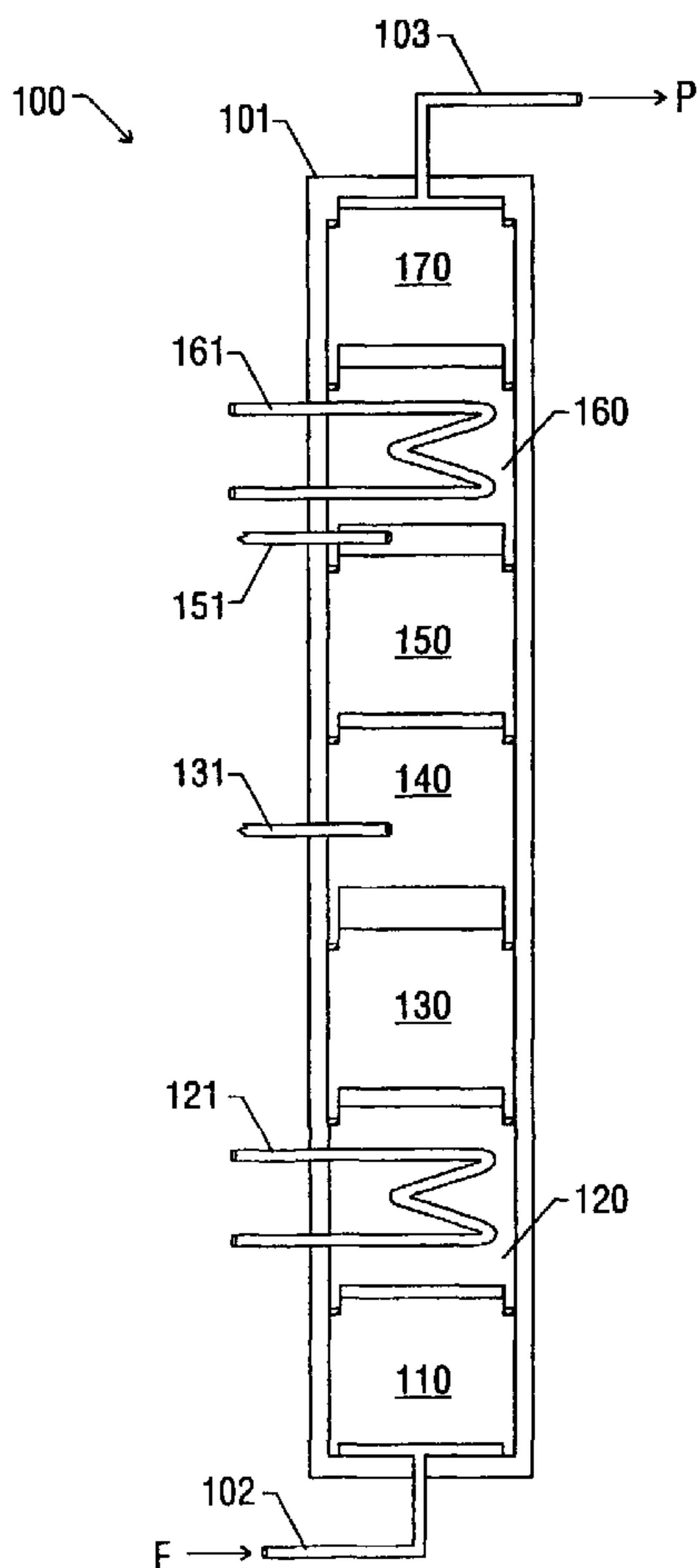
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(54) Title: COMPACT FUEL PROCESSOR FOR PRODUCING A HYDROGEN RICH GAS



(57) Abstract: An apparatus (100) including a plurality of modules stacked end-to-end along a common axis and a multi-step process of converting hydrocarbon fuel (F) to a substantially pure hydrogen gas (P) using said apparatus (100). Each module includes a shell having an interior space defining a passeway for the flow of gas from a first end of the shell to a second end of the shell opposite the first end, and a processing core being contained within the interior space for effecting a chemical, thermal, or physical change to a gas stream passing axially through the module. In one embodiment, said plurality of modules including a first module (110) containing a partial oxidation catalyst and steam reforming catalyst, a second module (120) containing a first heat exchanger (121), a third module (130) containing a desulfurization agent, a fourth module (140) containing an inert material for mixing components of gas stream passing there through, a fifth module (150) containing a water gas shift catalyst bed, a sixth module (160) containing a second heat exchanger (161) and a seventh module (170) containing a carbon monoxide oxidation catalyst bed.

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COMPACT FUEL PROCESSOR FOR PRODUCING A HYDROGEN RICH GAS

BACKGROUND OF THE INVENTION

1
2 Fuel cells provide electricity from chemical oxidation-reduction reactions and
3 possess significant advantages over other forms of power generation in terms of
4 cleanliness and efficiency. Typically, fuel cells employ hydrogen as the fuel and oxygen
5 as the oxidizing agent. The power generation is proportional to the consumption rate of
6 the reactants.

7 A significant disadvantage which inhibits the wider use of fuel cells is the lack of
8 a widespread hydrogen infrastructure. Hydrogen has a relatively low volumetric energy
9 density and is more difficult to store and transport than the hydrocarbon fuels currently
10 used in most power generation systems. One way to overcome this difficulty is the use of
11 reformers to convert the hydrocarbons to a hydrogen rich gas stream which can be used
12 as a feed for fuel cells.

13 Hydrocarbon-based fuels, such as natural gas, LPG, gasoline, and diesel, require
14 conversion processes to be used as fuel sources for most fuel cells. Current art uses multi-
15 step processes combining an initial conversion process with several clean-up processes.
16 The initial process is most often steam reforming (SR), autothermal reforming (ATR),
17 catalytic partial oxidation (CPOX), or non-catalytic partial oxidation (POX). The clean-
18 up processes are usually comprised of a combination of desulfurization, high temperature
19 water-gas shift, low temperature water-gas shift, selective CO oxidation, or selective CO
20 methanation. Alternative processes include hydrogen selective membrane reactors and
21 filters.

22 Despite the above work, there remains a need for a simple unit for converting a
23 hydrocarbon fuel to a hydrogen rich gas stream for use in conjunction with a fuel cell.

SUMMARY OF THE INVENTION

24
25
26 The present invention is generally directed to an apparatus and method for
27 converting hydrocarbon fuel into a hydrogen rich gas. In one illustrative embodiment of
28 the present invention, the apparatus for converting hydrocarbon fuel into hydrogen rich
29 gas includes a plurality of modules stacked end-to-end along a common axis. Each
30 module includes a shell having an interior space defining a passageway for the flow of
31 gas from a first end of the shell to a second end of the shell opposite the first end. The

1 apparatus further includes a processing core being contained within the interior space for
2 effecting a chemical, thermal, or physical change to a gas stream passing through the
3 processing core. It is a preferred aspect of the present invention that the modules are
4 cylindrical in shape. In one illustrative and preferred embodiment, each module includes
5 an annular lip at either the first end or the second end of the shell and an annular recessed
6 portion at the opposite end of the shell. This is designed such that the annular lip of one
7 module is receivable into the annular recess of the adjacent module.

8 Depending upon the reaction taking place within the module, each module may
9 include an annular layer of thermally insulating material disposed between the shell and
10 the respective processing core. In a similar manner, a module may include a porous
11 support member, such as screen, mesh, perforated plate, or porous sintered plate. Such a
12 porous support member may be included so as to support and contain the contents of the
13 module, particularly granular catalyst materials.

14 As noted above and described herein, the apparatus of the present invention is
15 used to carry out a series of reactions that converts hydrocarbon fuel to hydrogen rich
16 gas. In one illustrative embodiment of such an apparatus, the first module preferably has
17 a processing core that includes a partial oxidation catalyst or alternatively a steam
18 reforming catalyst or alternatively an autothermal reforming catalyst or alternatively
19 combinations and/or mixtures of such catalysts. A second module positioned adjacent to
20 the first module is preferably designed so that the processing core of the second module
21 includes a first heat exchanger. Such a heat exchanger may be a fin-typed heat
22 exchanger, tubing heat exchanger, heat pipe, or similar means that are capable of
23 exchanging heat.

24 Within the plurality of modules, a third module is preferably positioned adjacent
25 to the second module, the processing core of the third module including a desulfurizing
26 agent. A wide variety of desulfurizing agents may be used but preferably the
27 desulfurizing agent includes zinc oxide. A fourth module positioned adjacent to and in
28 fluid communication with the third module includes a processing core containing a water
29 gas shift catalyst. One of skill in the art should understand and appreciate that the water
30 gas shift catalyst may be a low temperature water gas shift catalyst that includes a
31 catalyst material selected from copper, copper oxide, zinc, platinum, rhenium, palladium,

1 rhodium, and gold and combinations and mixtures of these and similar materials.
2 Alternatively, the water gas shift catalyst is a high temperature water gas shift catalyst
3 that includes a catalyst material selected from ferric oxide, chromic oxide, copper, iron
4 silicide, platinum, palladium and other platinum group members, and combinations and
5 mixtures of these and similar materials.

6 The apparatus is further designed to include within the plurality of modules a fifth
7 module positioned adjacent to and in fluid communication with the fourth module. The
8 processing core of the fifth module includes a second heat exchanger. Such a heat
9 exchanger may include a fin-typed heat exchanger, tubing heat exchanger, heat pipe, or
10 similar means that are capable of exchanging heat.

11 The plurality of modules further includes a sixth module positioned adjacent to
12 the fifth module with which it is in fluid communication. The processing core of the sixth
13 module includes a carbon monoxide oxidation catalyst that preferably includes a material
14 selected from platinum, palladium, iron, chromium, manganese, iron oxide, chromium
15 oxide, manganese oxide, ruthenium, , gold, cerium, lanthanum, and combinations and
16 mixtures of these and similar compounds.

17 The present invention also includes a process for converting hydrocarbon fuel into
18 a hydrogen rich gas. One such illustrative process utilizes the apparatus disclosed herein.
19 Such a process generally includes providing a fuel processor having a plurality of
20 modules stacked end-to-end along a common axis, and feeding the hydrocarbon fuel
21 successively through each of the above described modules in an axial direction through a
22 tubular reactor to produce the hydrogen rich gas.

23

24

BRIEF DESCRIPTION OF THE DRAWINGS

25

26

The description is presented with reference to the accompanying drawings in
which:

27

28

FIG. 1 depicts a simple process flow diagram for one illustrative embodiment of
the present invention.

29

30

FIG. 2 illustrates one illustrative embodiment of the compact fuel processor
apparatus of the present invention; and

1 FIG. 3 is a cut-away partly sectional perspective view of a module employed in
2 the compact fuel processor apparatus.

3 4 **DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS**

5 The present invention is generally directed to an apparatus for converting
6 hydrocarbon fuel into a hydrogen rich gas. In a preferred aspect, the apparatus and
7 method described herein relate to a compact processor for producing a hydrogen rich gas
8 stream from a hydrocarbon fuel for use in fuel cells. However, other possible uses are
9 contemplated for the apparatus and method described herein, including any use wherein a
10 hydrogen rich stream is desired. Accordingly, while the invention is described herein as
11 being used in conjunction with a fuel cell, the scope of the invention is not limited to such
12 use.

13 Each of the illustrative embodiments of the present invention describe a fuel
14 processor or a process for using such a fuel processor with the hydrocarbon fuel feed
15 being directed through the fuel processor. The hydrocarbon fuel may be liquid or gas at
16 ambient conditions as long as it can be vaporized. As used herein the term
17 "hydrocarbon" includes organic compounds having C-H bonds which are capable of
18 producing hydrogen from a partial oxidation or steam reforming reaction. The presence
19 of atoms other than carbon and hydrogen in the molecular structure of the compound is
20 not excluded. Thus, suitable fuels for use in the method and apparatus disclosed herein
21 include, but are not limited to hydrocarbon fuels such as natural gas, methane, ethane,
22 propane, butane, naphtha, gasoline, and diesel fuel, and alcohols such as methanol,
23 ethanol, propanol, and the like.

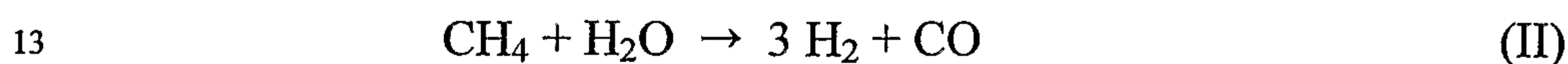
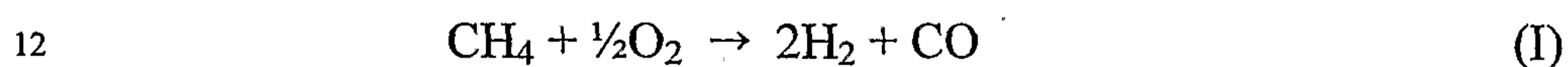
24 The fuel processor feeds include hydrocarbon fuel, oxygen, and water. The
25 oxygen can be in the form of air, enriched air, or substantially pure oxygen. The water
26 can be introduced as a liquid or vapor. The composition percentages of the feed
27 components are determined by the desired operating conditions, as discussed below.

28 The fuel processor effluent stream from of the present invention includes
29 hydrogen and carbon dioxide and can also include some water, unconverted
30 hydrocarbons, carbon monoxide, impurities (e.g. hydrogen sulfide and ammonia) and

1 inert components (e.g., nitrogen and argon, especially if air was a component of the feed
2 stream).

3 Figure 1 depicts a general process flow diagram illustrating the process steps
4 included in the illustrative embodiments of the present invention. One of skill in the art
5 should appreciate that a certain amount of progressive order is needed in the flow of the
6 reactants through the reactors disclosed herein.

7 Process step A is an autothermal reforming process in which two reactions, partial
8 oxidation (formula I, below) and optionally also steam reforming (formula II, below), are
9 combined to convert the feed stream F into a synthesis gas containing hydrogen and
10 carbon monoxide. Formulas I and II are exemplary reaction formulas wherein methane is
11 considered as the hydrocarbon:



14 The partial oxidation reaction occurs very quickly to the complete conversion of
15 oxygen added and produces heat. The steam reforming reaction occurs slower and
16 consumes heat. A higher concentration of oxygen in the feed stream favors partial
17 oxidation whereas a higher concentration of water vapor favors steam reforming.
18 Therefore, the ratios of oxygen to hydrocarbon and water to hydrocarbon become
19 characterizing parameters. These ratios affect the operating temperature and hydrogen
20 yield.

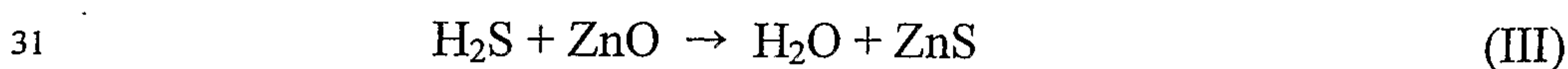
21 The operating temperature of the autothermal reforming step can range from
22 about 550°C to about 900°C, depending on the feed conditions and the catalyst. The
23 invention uses a catalyst bed of a partial oxidation catalyst with or without a steam
24 reforming catalyst. The catalyst may be in any form including pellets, spheres, extrudate,
25 monoliths, and the like. Partial oxidation catalysts should be well known to those with
26 skill in the art and are often comprised of noble metals such as platinum, palladium,
27 rhodium, and/or ruthenium on an alumina washcoat on a monolith, extrudate, pellet or
28 other support. Non-noble metals such as nickel or cobalt have been used. Other
29 washcoats such as titania, zirconia, silica, and magnesia have been cited in the literature.
30 Many additional materials such as lanthanum, cerium, and potassium have been cited in

1 the literature as “promoters” that improve the performance of the partial oxidation
2 catalyst.

3 Steam reforming catalysts should be known to those with skill in the art and can
4 include nickel with amounts of cobalt or a noble metal such as platinum, palladium,
5 rhodium, ruthenium, and/or iridium. The catalyst can be supported, for example, on
6 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination.
7 Alternatively, the steam reforming catalyst can include nickel, preferably supported on
8 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination,
9 promoted by an alkali metal such as potassium.

10 Process step B is a cooling step for cooling the synthesis gas stream from process
11 step A to a temperature of from about 200°C to about 600°C, preferably from about
12 300°C to about 500°C, and more preferably from about 375°C to about 425°C, to
13 optimize the temperature of the synthesis gas effluent for the next step. This cooling may
14 be achieved with heat sinks, heat pipes or heat exchangers depending upon the design
15 specifications and the need to recover / recycle the heat content of the gas stream. One
16 illustrative embodiment for step B is the use of a heat exchanger utilizing feed stream F
17 as the coolant circulated through the heat exchanger. The heat exchanger can be of any
18 suitable construction known to those with skill in the art including shell and tube, plate,
19 spiral, etc. Alternatively, or in addition thereto, cooling step B may be accomplished by
20 injecting additional feed components such as fuel, air or water. Water is preferred
21 because of its ability to absorb a large amount of heat as it is vaporized to steam. The
22 amounts of added components depend upon the degree of cooling desired and are readily
23 determined by those with skill in the art.

24 Process step C is a purifying step. One of the main impurities of the hydrocarbon
25 stream is sulfur, which is converted by the autothermal reforming step A to hydrogen
26 sulfide. The processing core used in process step C preferably includes zinc oxide and/or
27 other material capable of absorbing and converting hydrogen sulfide, and may include a
28 support (e.g., monolith, extrudate, pellet etc.). Desulfurization is accomplished by
29 converting the hydrogen sulfide to water in accordance with the following reaction
30 formula III:



1 Other impurities such as chlorides can also be removed. The reaction is
2 preferably carried out at a temperature of from about 300°C to about 500°C, and more
3 preferably from about 375°C to about 425°C. Zinc oxide is an effective hydrogen sulfide
4 absorbent over a wide range of temperatures from about 25°C to about 700°C and affords
5 great flexibility for optimizing the sequence of processing steps by appropriate selection
6 of operating temperature.

7 The effluent stream may then be sent to a mixing step D in which water is
8 optionally added to the gas stream. The addition of water lowers the temperature of the
9 reactant stream as it vaporizes and supplies more water for the water gas shift reaction of
10 process step E (discussed below). The water vapor and other effluent stream components
11 are mixed by being passed through a processing core of inert materials such as ceramic
12 beads or other similar materials that effectively mix and/or assist in the vaporization of
13 the water. Alternatively, any additional water can be introduced with feed, and the
14 mixing step can be repositioned to provide better mixing of the oxidant gas in the CO
15 oxidation step G disclosed below.

16 Process step E is a water gas shift reaction that converts carbon monoxide to
17 carbon dioxide in accordance with formula IV:



19 This is an important step because carbon monoxide, in addition to being highly
20 toxic to humans, is a poison to fuel cells. The concentration of carbon monoxide should
21 preferably be lowered to a level that can be tolerated by fuel cells, typically below 50
22 ppm. Generally, the water gas shift reaction can take place at temperatures of from
23 150°C to 600°C depending on the catalyst used. Under such conditions, most of the
24 carbon monoxide in the gas stream is converted in this step.

25 Low temperature shift catalysts operate at a range of from about 150°C to about
26 300°C and include for example, copper oxide, or copper supported on other transition
27 metal oxides such as zirconia, zinc supported on transition metal oxides or refractory
28 supports such as silica, alumina, zirconia, etc., or a noble metal such as platinum,
29 rhenium, palladium, rhodium or gold on a suitable support such as silica, alumina,
30 zirconia, and the like.

1 High temperature shift catalysts are preferably operated at temperatures ranging
2 from about 300° to about 600°C and can include transition metal oxides such as ferric
3 oxide or chromic oxide, and optionally including a promoter such as copper or iron
4 silicide. Also included, as high temperature shift catalysts are supported noble metals
5 such as supported platinum, palladium and/or other platinum group members.

6 The processing core utilized to carry out this step can include a packed bed of
7 high temperature or low temperature shift catalyst such as described above, or a
8 combination of both high temperature and low temperature shift catalysts. The process
9 should be operated at any temperature suitable for the water gas shift reaction, preferably
10 at a temperature of from 150°C to about 400°C depending on the type of catalyst used.
11 Optionally, a cooling element such as a cooling coil may be disposed in the processing
12 core of the shift reactor to lower the reaction temperature within the packed bed of
13 catalyst. Lower temperatures favor the conversion of carbon monoxide to carbon
14 dioxide. Also, a purification processing step C can be performed between high and low
15 shift conversions by providing separate steps for high temperature and low temperature
16 shift with a desulfurization module between the high and low temperature shift steps.

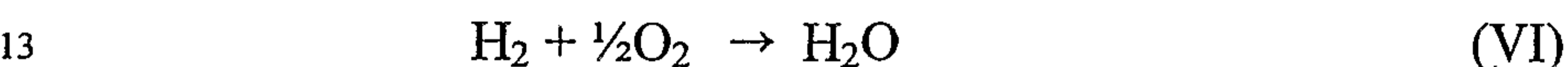
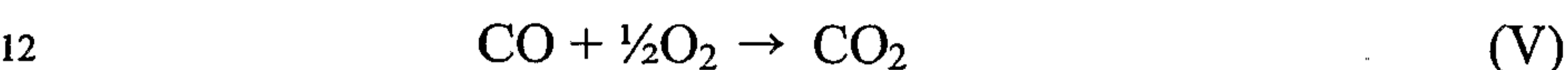
17 Process step F is a cooling step performed in one embodiment by a heat
18 exchanger. The heat exchanger can be of any suitable construction including shell and
19 tube, plate, spiral, etc. Alternatively a heat pipe or other form of heat sink may be
20 utilized. The goal of the heat exchanger is to reduce the temperature of the gas stream to
21 produce an effluent having a temperature preferably in the range of from about 90°C to
22 about 150°C.

23 Oxygen is added to the process in step F. The oxygen is consumed by the
24 reactions of process step G described below. The oxygen can be in the form of air,
25 enriched air, or substantially pure oxygen. The heat exchanger may by design provide
26 mixing of the air with the hydrogen rich gas. Alternatively, the embodiment of process
27 step D may be used to perform the mixing.

28 Process step G is an oxidation step wherein almost all of the remaining carbon
29 monoxide in the effluent stream is converted to carbon dioxide. The processing is carried
30 out in the presence of a catalyst for the oxidation of carbon monoxide and may be in any
31 suitable form, such as pellets, spheres, monolith, etc. Oxidation catalysts for carbon

1 monoxide are known and typically include noble metals (e.g., platinum, palladium)
2 and/or transition metals (e.g., iron, chromium, manganese), and/or compounds of noble
3 or transition metals, particularly oxides. A preferred oxidation catalyst is platinum on an
4 alumina washcoat. The washcoat may be applied to a monolith, extrudate, pellet or other
5 support. Additional materials such as cerium or lanthanum may be added to improve
6 performance. Many other formulations have been cited in the literature with some
7 practitioners claiming superior performance from rhodium or alumina catalysts.
8 Ruthenium, palladium, gold, and other materials have been cited in the literature as being
9 active for this use.

10 Two reactions occur in process step G: the desired oxidation of carbon monoxide
11 (formula V) and the undesired oxidation of hydrogen (formula VI) as follows:



14 The preferential oxidation of carbon monoxide is favored by low temperatures. Since
15 both reactions produce heat it may be advantageous to optionally include a cooling
16 element such as a cooling coil disposed within the process. The operating temperature of
17 process is preferably kept in the range of from about 90°C to about 150°C. Process step
18 G preferably reduces the carbon monoxide level to less than 50 ppm, which is a suitable
19 level for use in fuel cells, but one of skill in the art should appreciate that the present
20 invention can be adapted to produce a hydrogen rich product with of higher and lower
21 levels of carbon monoxide.

22 The effluent exiting the fuel processor is a hydrogen rich gas containing carbon
23 dioxide and other constituents which may be present such as water, inert components
24 (e.g., nitrogen, argon), residual hydrocarbon, etc. Product gas may be used as the feed for
25 a fuel cell or for other applications where a hydrogen rich feed stream is desired.
26 Optionally, product gas may be sent on to further processing, for example, to remove the
27 carbon dioxide, water or other components.

28 In one illustrative embodiment of the present invention, the fuel processor is of
29 modular construction with individual modular units, which are separable, rearrangeable,
30 and individually replaceable. Referring to Figure 2, the fuel processor 100 of the present
31 invention includes a series of individual modules (110, 120, 130, 140, 150, 160 and 170).

1 The modular units may be used in any orientation, e.g., vertical or horizontal orientation,
2 and is adapted to be used in conjunction with a fuel cell such that the hydrogen rich
3 product gas of the reactor described herein is supplied directly to a fuel cell as a feed
4 stream. While the modules can have any cross sectional configuration, such as circular,
5 rectangular, triangular, etc., a circular cross section is preferred with the fuel processor
6 100 being of a generally tubular shape.

7 The modules are constructed in accordance with the description given below in
8 connection with Figure 3, unless indicated otherwise. The modules can be fabricated
9 from any material capable of withstanding the operating conditions and chemical
10 environment of the reactions described herein and can include, for example, stainless
11 steel, Inconel, Incoloy, Hastelloy, and the like. The reaction pressure is preferable from
12 about 0 to about 100 psig, although higher pressures may be employed. The operating
13 pressure of the fuel processor depends upon the delivery pressure required by the fuel
14 cell. For fuel cells operating in the 1 to 20 kW range an operating pressure of 0 to about
15 100 psig is generally sufficient. The modules are of such dimensions so as to safely
16 contain the reaction at the desired operating pressures and temperatures.

17 Fuel processor 100 as shown in Figure 2 effects the process diagrammatically
18 illustrated in Figure 1. Feed stream F is introduced through inlet pipe 102 and product
19 gas P is drawn off via outlet pipe 103. The apparatus 100 includes several modules that
20 may be stacked to form a modular assembly that can be modified by the replacement of
21 individual modules. Each module performs a separate operational function and is
22 generally configured as shown in Figure 2. Module 110 is the autothermal reforming
23 module corresponding to process step A of Figure 1. Module 120 is a cooling step
24 corresponding to process step B of Figure 1. In this illustrative embodiment, heat
25 exchanger 121 is shown as a general heat sink for Module 120. Module 130 is a
26 purifying module corresponding to process step C of Figure 1. Module 140 is an optional
27 mixing step corresponding to process step D of Figure 1. Feed nozzle 131 provides an
28 optional water stream feed to Module 140 to aid in driving the water gas shift reaction
29 (Equation IV) of Module 150. Module 150 is a water gas shift module corresponding to
30 process step E of Figure 1. Feed nozzle 151 provides a source for oxygen to process gas
31 for the oxidation reaction (Equation V) of Module 170. Module 150 also contains a heat

1 exchanger (not shown) positioned within or surrounding the catalyst bed so as to
2 maintain a desired water gas shift reaction temperature. Module 160 is a cooling step
3 corresponding to process step F of Figure 1. In this illustrative embodiment, heat
4 exchanger 161 is shown as a general heat sink for Module 160. Module 170 is an
5 oxidation step corresponding to process step G of Figure 1. Module 170 also contains a
6 heat exchanger (not shown) positioned within or surrounding the catalyst bed so as to
7 maintain a desired oxidation reaction temperature. One of skill in the art should
8 appreciate that the process configuration described in this embodiment may vary
9 depending on numerous factors, including but not limited to feedstock quality and
10 required product quality.

11 Figure 3 illustrates an individual module 10 that includes a shell 11, an optional
12 support plate 12, an annular gasket 13, an optional insulative material 14, and a
13 processing core 15. Shell 11 can have any cross sectional shape such as circular, square,
14 triangular, etc. However shell 11 is preferably a cylindrical shaped tubular member
15 having an axial bore. Shell 11 is preferably fabricated from a material such as stainless
16 steel, Inconel, Incoloy, or Hastelloy for the reasons stated above. Shell 11 includes an
17 annular upper recess 11a and an annular lower lip 11b, which serve as mating features to
18 facilitate the stacking of two or more modules. The upper recess 11a is adapted to
19 receive gasket 13 and lower lip 11b.

20 The optional support plate 12 is preferably fabricated from, for example, a screen,
21 mesh, perforated plate, porous sintered metal plate, and the like. It can be fabricated
22 from metal alloys such as stainless steel, Inconel, Incoloy, or Hastelloy, or from a suitable
23 ceramic material. The support plate 12 not only provides support for the components
24 contained within the module 10, it also serves as a gas distributor to distribute the gas
25 flow through the reactor evenly throughout the cross section of the reactor. Even
26 distribution of the gas facilitates optimal performance of the reactor.

27 Gasket 13 is a ring shaped piece to help seal the joint between modules and
28 prevent gas leaks. It can be fabricated from materials such as graphite, ceramic, copper,
29 or other materials capable of withstanding the operating conditions of the reactor.

30 Optional internal insulator 14 is disposed within the axial bore of cylindrical shell
31 11 and comprises a cylindrical piece with an axial bore. Insulator 14 minimizes heat loss

1 to the environment that could reduce the system efficiency. It shortens start-up time and
2 reduces heat transfer to the shell 11 and the environment. Internal insulator 14 can be
3 fabricated from any material suitable for the purposes described herein. Preferred
4 materials include interam intumescent fibrous ceramic mat; saffil alumina fibrous mat;
5 flexible, knitted steel wire mat (such as Wire Wrap); and other flexible ceramic mats
6 made from alumina or silica fibers and similar such materials.

7 Processing core 15 is contained within the axial bore of shell 11, and, if the
8 internal insulator 14 is present, also within the bore of the internal insulator. Processing
9 core 15 accomplishes the function of the module and can be a catalyst, adsorbent,
10 absorbent, heat exchanger, or inert material.

11 Such a skilled person in the art should also appreciate that the present invention
12 also encompasses the following illustrative embodiments. One such illustrative
13 embodiment includes an apparatus for converting hydrocarbon fuel into a hydrogen rich
14 gas, comprising a plurality of modules stacked end-to-end along a common axis, wherein
15 each module includes a shell having an interior space defining a passageway for the flow
16 of gas from a first end of the shell to a second end of the shell opposite the first end, and a
17 processing core being contained within the interior space for effecting a chemical,
18 thermal, or physical change to a gas stream passing axially therethrough. Such an
19 apparatus may include an outer housing within which the plurality of modules are
20 disposed. Whereas this apparatus is intended to encompass numerous shapes and
21 orientations, a preferred aspect of the present apparatus is for the optional outer housing
22 and the modules to be cylindrical in shape. Numerous means exist for connecting the
23 modules together to form the apparatus of the present invention. However, a preferred
24 aspect of the present invention is for each module includes an annular lip at either the
25 first end or the second end of the shell and an annular recessed portion at the opposite end
26 of the shell, whereby the annular lip of one module is receivable into the annular recess
27 of the adjacent module. A preferred aspect of the present invention is for one or more of
28 the modules to include an annular layer of thermally insulative material disposed between
29 the shell and the respective processing core. At least one module includes a porous
30 support member mounted in proximity to one end of the shell, where the porous support

1 member is selected from the group consisting of a screen, mesh, perforated plate, and
2 porous sintered plate.

3 Another illustrative embodiment of the present invention is an apparatus for
4 converting hydrocarbon fuel into a hydrogen rich gas, comprising a plurality of modules
5 stacked end-to-end along a common axis, wherein each module includes a shell having an
6 interior space defining a passageway for the flow of gas from a first end of the shell to a
7 second end of the shell opposite the first end, and a processing core being contained
8 within the interior space for effecting a chemical, thermal, or physical change to a gas
9 stream passing axially therethrough. The first module contains a processing core that
10 includes a partial oxidation catalyst. The partial oxidation catalyst can include a metal
11 such as platinum, palladium, rhodium, ruthenium, nickel, cobalt, or any combination
12 thereof. Optionally, the first module may also contain a steam reforming catalyst. The
13 steam reforming catalyst can include a metal such as platinum, palladium, rhodium,
14 ruthenium, iridium, nickel, potassium, or any combination thereof. The partial oxidation
15 catalyst may be supported on a material such as magnesia, alumina, titania, zirconia, or
16 silica. The steam reforming catalyst may be supported on a material such as magnesia,
17 alumina, silica, zirconia, or magnesium aluminate. The second module, which is
18 positioned adjacent to the first module, contains a heat exchanger inside the processing
19 core for cooling the gas stream produced from the first module. The third module, which
20 is positioned adjacent to the second module, contains a desulfurization agent, such as zinc
21 oxide, inside the processing core. Optionally, a fourth module may be included,
22 positioned adjacent to the third module, and would contain an inert material such as
23 ceramic beads for mixing water and components of the process gas stream. If no fourth
24 module is included in the apparatus, water should be added prior to the fifth module. The
25 fifth module, which is positioned adjacent to the fourth module or the third module if no
26 fourth module is included, contains a water gas shift catalyst inside the processing core.
27 It is intended by the present invention that a low temperature water gas shift catalyst, a
28 high temperature water gas shift catalyst, or a combination of the two can be utilized in
29 the fifth module. Possible low temperature water gas shift catalysts include copper,
30 copper oxide, zinc, platinum, rhenium, palladium, rhodium, and gold. Possible high
31 temperature water gas shift catalyst includes a material selected from the group consisting

1 of ferric oxide, chromic oxide, copper, iron silicide, platinum, and palladium. The fifth
2 module also includes a heat exchanger positioned within the water gas shift catalyst bed
3 for maintaining a desired shift reaction temperature range. The sixth module, which is
4 positioned adjacent to the fifth module, contains a heat exchanger inside the processing
5 core for cooling the gas stream produced by the fifth module. The seventh module,
6 which is positioned adjacent to the sixth module, contains a carbon monoxide oxidation
7 catalyst in the processing core. Such a carbon monoxide oxidation catalyst can be
8 platinum, palladium, iron, chromium, manganese, iron oxide, chromium oxide,
9 manganese oxide, ruthenium, palladium, gold, or any combination thereof. The seventh
10 module also includes a heat exchanger positioned within the water gas shift catalyst bed
11 for maintaining a desired oxidation reaction temperature range.

12 Yet another illustrative embodiment for the present invention is a process for
13 converting hydrocarbon fuel into a hydrogen rich gas by using a fuel processor having a
14 plurality of modules stacked end-to-end along a common axis, and by feeding the
15 hydrocarbon fuel successively through each of the modules in an axial direction to
16 produce the hydrogen rich gas. A first module, which may be designed according to the
17 previous illustrative embodiment for partial oxidation and steam reforming of the
18 hydrocarbon fuel, operates at a temperature ranging from about 550°C to about 900°C. A
19 second module, which may be designed according to the previous illustrative
20 embodiment, then cools the first module effluent to a temperature of from about 200°C to
21 about 600°C. The third module, which may be designed according to the previous
22 illustrative embodiment, desulfurizes the second module effluent using zinc oxide as a
23 desulfurizing agent. The optional fourth module, which may be designed according to
24 the previous illustrative embodiment, mixes water with the third module effluent to
25 produce a feed for the fifth module. The fifth module, which may be designed according
26 to the previous illustrative embodiment, reacts water and the carbon monoxide contained
27 in process stream in a water gas shift reaction to reduce the carbon monoxide
28 concentration leaving the fifth module. A preferred aspect of the present invention is that
29 the fifth module operates at a temperature ranging from about 150°C to about 400°C.
30 The sixth module, which may be designed according to the previous illustrative
31 embodiment, cools the fifth module effluent to a temperature of from about 90°C to about

1 150°C. The seventh module, which may be designed according to the previous
2 illustrative embodiment, oxidizes at least some carbon monoxide in the process gas
3 stream to produce the hydrogen rich gas. A preferred aspect of the present invention is
4 that the seventh module operates at a temperature of from about 90°C to about 150°C.
5 One additional aspect of the present invention is the potential for heat integration. In
6 terms of the present embodiment, heat exchange in the second module, fifth module,
7 sixth module, and seventh module may be utilized to preheat the hydrocarbon feed to the
8 apparatus. It is intended that the present invention be able to reduce the carbon monoxide
9 concentration in the hydrogen rich gas to less than 50 ppm.

10 While the apparatus, compositions and methods of this invention have been
11 described in terms of preferred or illustrative embodiments, it will be apparent to those of
12 skill in the art that variations may be applied to the process described herein without
13 departing from the concept and scope of the invention. All such similar substitutes and
14 modifications apparent to those skilled in the art are deemed to be within the scope and
15 concept of the invention as it is set out in the following claims.

1 **WHAT IS CLAIMED IS:**

- 2
- 3 1. An apparatus for converting hydrocarbon fuel into a hydrogen rich gas, comprising a
4 plurality of modules stacked end-to-end along a common axis, wherein each module
5 of the plurality of modules includes:
6 a shell having an interior space defining a passageway for the flow of a gas stream
7 from a first end of the shell to a second end of the shell opposite the first end, and
8 a processing core being contained within the interior space for effecting a chemical,
9 thermal, or physical change to the gas stream passing axially therethrough.
- 10
- 11 2. The apparatus as described in claim 1, wherein the plurality of modules are
12 cylindrical in shape.
- 13
- 14 3. The apparatus as described in claim 1, wherein each module of the plurality of
15 modules includes an annular lip at either the first end or the second end of the shell
16 and an annular recessed portion at the opposite end of the shell, and wherein the
17 annular lip of one module is receivable into the annular recess of the adjacent module.
- 18
- 19 4. The apparatus as described in claim 1, wherein at least one module of the plurality of
20 modules includes an annular layer of thermally insulative material disposed between
21 the shell and the respective processing core.
- 22
- 23 5. The apparatus as described in claim 1, wherein at least one module of the plurality of
24 modules includes a porous support member mounted in proximity to the first end of
25 the shell.
- 26
- 27 6. The apparatus as described in claim 1, wherein at least one module of the plurality of
28 modules includes a porous support member mounted in proximity to the second end
29 of the shell.
- 30

- 1 7. The apparatus as described in claim 6, wherein the porous support member is selected
2 from the group consisting of a screen, mesh, perforated plate, and porous sintered
3 plate.
4
- 5 8. The apparatus as described in claim 1, wherein the plurality of modules includes a
6 first module, wherein the processing core of the first module includes a partial
7 oxidation catalyst.
8
- 9 9. The apparatus as described in claim 8, wherein the first module also includes a steam
10 reforming catalyst.
11
- 12 10. The apparatus as described in claim 8, wherein the partial oxidation catalyst includes
13 a metal selected from the group consisting of platinum, palladium, rhodium,
14 ruthenium, nickel, cobalt, and any combinations thereof.
15
- 16 11. The apparatus as described in claim 9, wherein the steam reforming catalyst includes
17 a metal selected from the group consisting of platinum, palladium, rhodium,
18 ruthenium, iridium, nickel, potassium, and combinations thereof.
19
- 20 12. The apparatus as described in claim 10, wherein the metal of the partial oxidation
21 catalyst is supported on a material selected from the group consisting of magnesia,
22 alumina, titania, zirconia, and silica.
23
- 24 13. The apparatus as described in claim 11, wherein the metal of the steam reforming
25 catalyst is supported on a material selected from the group consisting of magnesia,
26 alumina, silica, zirconia, and magnesium aluminate.
27
- 28 14. The apparatus as described in claim 1, wherein the plurality of modules includes a
29 second module, wherein the processing core of the second module includes a first
30 heat exchanger for cooling the gas stream.
31

1 15. The apparatus as described in claim 1, wherein the plurality of modules includes a
2 third module, wherein the processing core of the third module includes a
3 desulfurization agent.

4

5 16. The apparatus as described in claim 14, wherein the desulfurization agent includes
6 zinc oxide.

7

8 17. The apparatus as described in claim 1, wherein the plurality of modules includes a
9 fourth module, wherein the processing core of the fourth module includes an inert
10 material for mixing components of the gas stream passing therethrough.

11

12 18. The apparatus as described in claim 17, wherein the inert material comprises ceramic
13 beads.

14

15 19. The apparatus as described in claim 17, wherein the fourth module is designed to
16 introduce water to the gas stream.

17

18 20. The apparatus as described in claim 1, wherein the plurality of modules includes a
19 fifth module, wherein the processing core of the fifth module includes:
20 a water gas shift catalyst bed; and
21 a heat exchanger positioned within the water gas shift catalyst bed for maintaining a
22 desired shift reaction temperature range.

23

24 21. The apparatus as described in claim 20, wherein the water gas shift catalyst is a low
25 temperature water gas shift catalyst.

26

27 22. The apparatus as described in claim 21 wherein the low temperature water gas shift
28 catalyst includes a material selected from the group consisting of copper, copper
29 oxide, zinc, platinum, rhenium, palladium, rhodium, and gold.

30

1 23. The apparatus as described in claim 20, wherein the water gas shift catalyst is a high
2 temperature water gas shift catalyst.

3

4 24. The apparatus as described in claim 23, wherein the high temperature water gas shift
5 catalyst includes a material selected from the group consisting of ferric oxide,
6 chromic oxide, copper, iron silicide, platinum, and palladium.

7

8 25. The apparatus as described in claim 1, wherein the plurality of modules includes a
9 sixth module, wherein the processing core of the sixth module includes a second heat
10 exchanger for cooling the gas stream.

11

12 26. The apparatus as described in claim 1, wherein the plurality of modules includes a
13 seventh module, wherein the processing core of the seventh module includes:
14 a carbon monoxide oxidation catalyst bed; and
15 a heat exchanger positioned within the carbon monoxide oxidation catalyst bed for
16 maintaining a desired oxidation reaction temperature range.

17

18 27. The apparatus as described in claim 26, wherein the seventh module is designed to
19 introduce an oxygen-containing stream to the gas stream prior to contact with the
20 carbon monoxide oxidation bed.

21

22 28. The apparatus as described in claim 26, wherein the carbon monoxide oxidation
23 catalyst bed includes a material selected from the group consisting of platinum,
24 palladium, iron, chromium, manganese, iron oxide, chromium oxide, manganese
25 oxide, ruthenium, palladium, gold, and any combinations thereof.

26

- 1 29. An apparatus for converting hydrocarbon fuel into a hydrogen rich gas, comprising a
2 plurality of modules stacked end-to-end along a common axis;
3 wherein each module of the plurality of modules includes:
4 a shell having an interior space defining a passageway for the flow of a gas stream
5 from a first end of the shell to a second end of the shell opposite the first end,
6 and
7 a processing core being contained within the interior space for effecting a
8 chemical, thermal, or physical change to the gas stream passing axially
9 therethrough; and
10 wherein the plurality of modules includes:
11 a first module containing a partial oxidation catalyst bed,
12 a second module positioned adjacent to the first module containing a first heat
13 exchanger for cooling the gas stream,
14 a third module positioned adjacent to the second module containing a
15 desulfurization agent,
16 a fourth module positioned adjacent the third module containing an inert material
17 for mixing components of the gas stream passing therethrough,
18 a fifth module positioned adjacent to the fourth module containing a water gas
19 shift catalyst bed,
20 a sixth module positioned adjacent to the fifth module containing a second heat
21 exchanger for cooling the gas stream, and
22 a seventh module positioned adjacent to the sixth module containing a carbon
23 monoxide oxidation catalyst bed.

1 30. An apparatus for converting hydrocarbon fuel into a hydrogen rich gas, comprising a
2 plurality of modules stacked end-to-end along a common axis;

3 wherein each module of the plurality of modules includes:

4 a shell having an interior space defining a passageway for the flow of a gas stream
5 from a first end of the shell to a second end of the shell opposite the first end,
6 and

7 a processing core being contained within the interior space for effecting a
8 chemical, thermal, or physical change to the gas stream passing axially
9 therethrough; and

10 wherein the plurality of modules includes:

11 a first module containing a partial oxidation catalyst bed,

12 a second module positioned adjacent to the first module containing a first heat
13 exchanger for cooling the gas stream,

14 a third module positioned adjacent to the second module containing a
15 desulfurization agent,

16 a fourth module positioned adjacent to the third module containing a water gas
17 shift catalyst bed,

18 a fifth module positioned adjacent to the fourth module containing a second heat
19 exchanger for cooling the gas stream, and

20 a sixth module positioned adjacent to the fifth module containing a carbon
21 monoxide oxidation catalyst bed.

22
23 31. A process for converting hydrocarbon fuel into a hydrogen rich gas comprising:

24 providing a fuel processor having a plurality of modules stacked end-to-end along a
25 common axis; and

26 feeding the hydrocarbon fuel successively through each of the modules in an axial
27 direction to produce the hydrogen rich gas.

28
29 32. The process as described in claim 31, wherein the plurality of modules includes:

30 a first module for the partial oxidation and steam reforming of the hydrocarbon
31 fuel to produce a first module effluent;

- 1 a second module positioned adjacent to the first module for cooling the first
2 module effluent to produce a second module effluent;
- 3 a third module positioned adjacent to the second module, wherein the third
4 module desulfurizes the second module effluent to produce a third module
5 effluent;
- 6 a fourth module positioned adjacent the third module, wherein the fourth module
7 mixes water with the third module effluent to produce a fourth module
8 effluent;
- 9 a fifth module positioned adjacent to the fourth module, wherein the fifth module
10 reacts the water and the carbon monoxide contained in the fourth module
11 effluent to produce a fifth module effluent having a reduced carbon monoxide
12 concentration;
- 13 a sixth module positioned adjacent to the fifth module for cooling the fifth module
14 effluent to produce a sixth module effluent;
- 15 a seventh module positioned adjacent to the sixth module for oxidizing at least
16 some carbon monoxide to produce the hydrogen rich gas.

17

18 33. The process as described in claims 32, wherein the hydrocarbon fuel may be
19 preheated by the second module, the fifth module, the sixth module, the seventh
20 module, or any combination thereof.

21

22 34. The process as described in claims 32, wherein the first module operates at a
23 temperature ranging from about 550°C to about 900°C.

24

25 35. The process as described in claim 32, wherein the second module effluent is from
26 about 200°C to about 600°C.

27

28 36. The process as described in claim 32, wherein the fifth module operates at a
29 temperature ranging from about 150°C to about 400°C.

30

1 37. The process as described in claim 32, wherein the fifth module effluent is cooled to a
2 temperature of from about 90°C to about 150°C.

3
4 38. The process as described in claim 32, wherein the seventh module operates at a
5 temperature of from about 90°C to about 150°C.

6
7 The process as described in claim 32, wherein the hydrogen rich gas contains less
8 than 50 ppm carbon monoxide.

9
10 39. The process as described in claim 31, wherein the plurality of modules includes:

11 a first module for the partial oxidation and steam reforming of the hydrocarbon
12 fuel to produce a first module effluent;

13 a second module positioned adjacent to the first module for cooling the first
14 module effluent to produce a second module effluent;

15 a third module positioned adjacent to the second module, wherein the third
16 module desulfurizes the second module effluent to produce a third module
17 effluent;

18 a fourth module positioned adjacent to the third module, wherein the fourth
19 module reacts water and the carbon monoxide contained in the third module
20 effluent to produce a fourth module effluent having a reduced carbon
21 monoxide concentration;

22 a fifth module positioned adjacent to the fourth module for cooling the fourth
23 module effluent to produce a fifth module effluent;

24 a sixth module positioned adjacent to the fifth module for oxidizing at least some
25 carbon monoxide to produce the hydrogen rich gas.

26
27 40. The process as described in claims 39, wherein the hydrocarbon fuel may be
28 preheated by the second module, the fourth module, the fifth module, the sixth
29 module, or any combination thereof.
30

- 1 41. The process as described in claims 39, wherein the first module operates at a
2 temperature ranging from about 550°C to about 900°C.
3
- 4 42. The process as described in claim 39, wherein the second module effluent is from
5 about 200°C to about 600°C.
6
- 7 43. The process as described in claim 39, wherein the fourth module operates at a
8 temperature ranging from about 150°C to about 400°C.
9
- 10 44. The process as described in claim 39, wherein the fourth module effluent is cooled to
11 a temperature of from about 90°C to about 150°C.
12
- 13 45. The process as described in claim 39, wherein the sixth module operates at a
14 temperature of from about 90°C to about 150°C.
15
- 16 46. The process as described in claim 39, wherein the hydrogen rich gas contains less
17 than 50 ppm carbon monoxide.

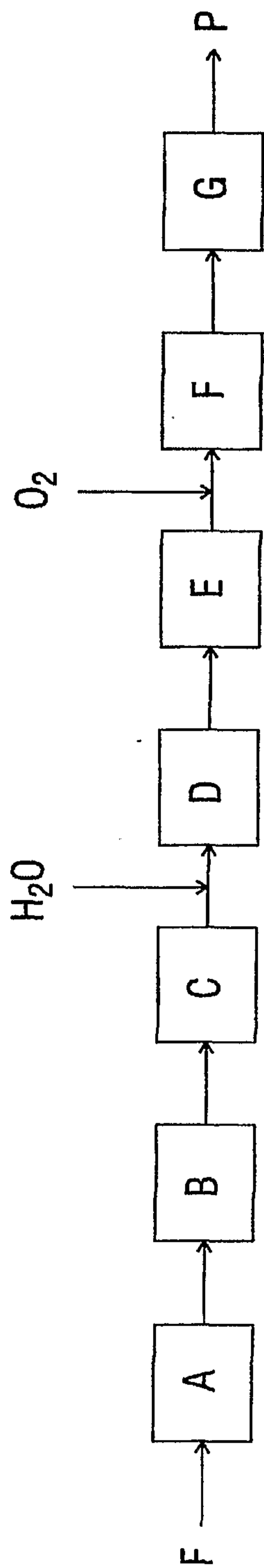


FIG. 1

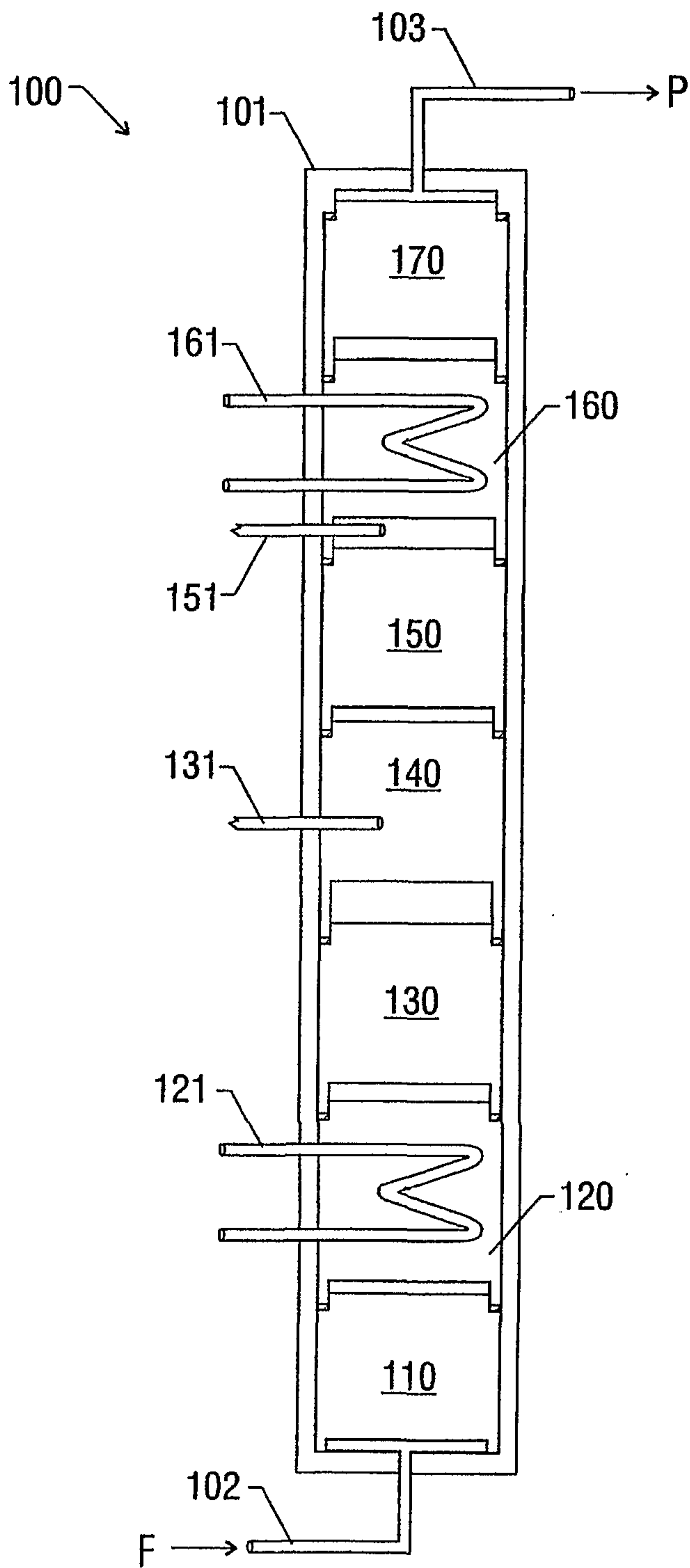


FIG. 2

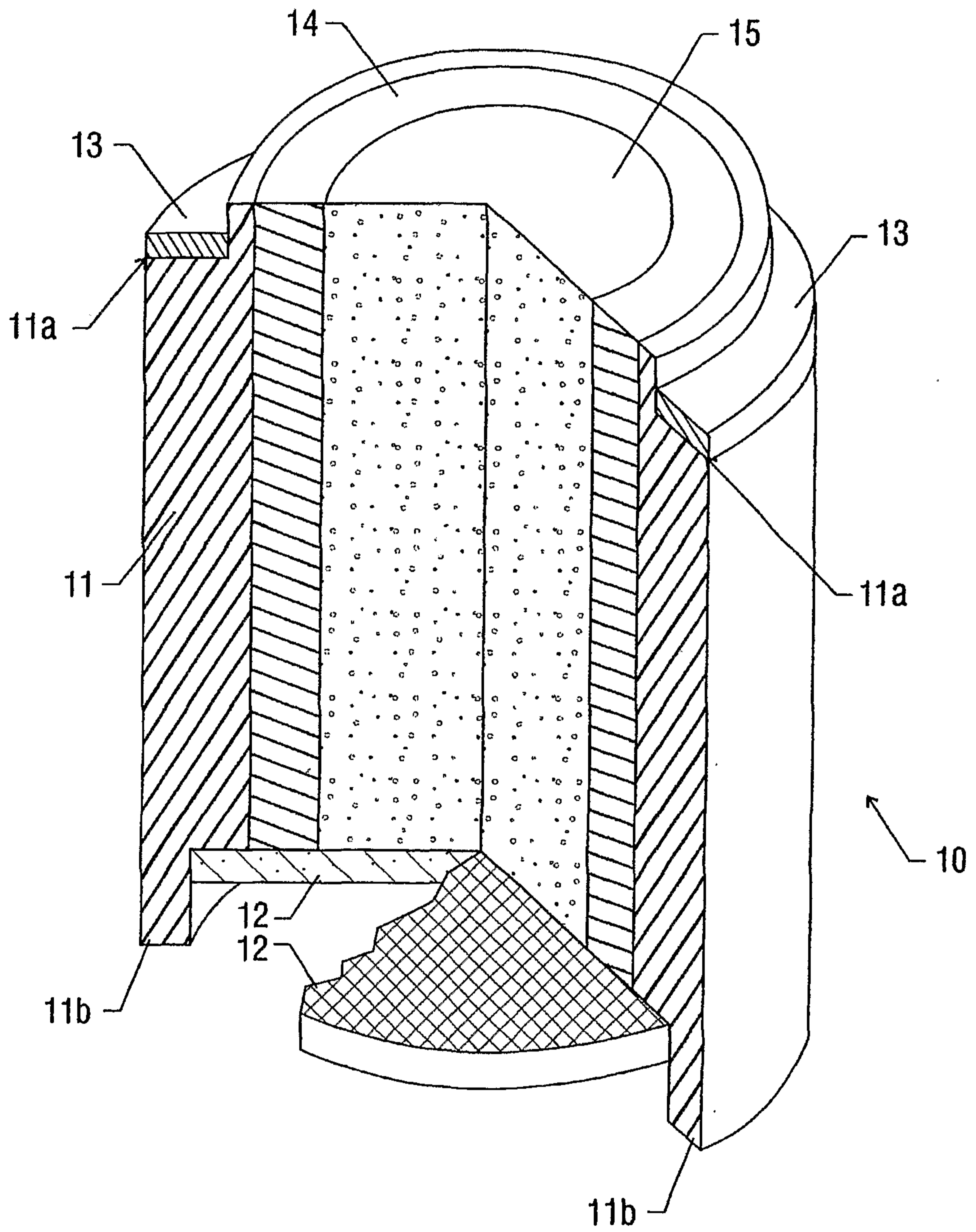


FIG. 3

