(54) Title: FLUIDIZED BED MEMBRANE REACTOR

FIG. 1

(57) Abstract: Herein disclosed is a dry reforming reactor comprising a gas inlet near the bottom of the reactor; a gas outlet near the top of the reactor; a fluidized bed comprising a catalyst; and one or more hydrogen membranes comprising palladium (Pd). In some cases, the one or more hydrogen membranes comprises Pd alloy membranes, or Pd supported on ceramics or metals. In some cases, the one or more hydrogen membranes are placed vertically in the reactor as hydrogen membrane tubes hanging from the top of the reactor. In some cases, the hydrogen membranes are configured to selectively collect hydrogen from the tubes via one or more internal manifolds and sent to an external hydrogen collection system.

UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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FLUIDIZED BED MEMBRANE REACTOR

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001]   Not applicable.

BACKGROUND

Field of the Invention

[0002]   This disclosure relates generally to fluidized bed membrane reactors.   More particularly, this disclosure relates to fluidized bed membrane reactors for dry reforming.

Background of Invention

[0003] Dry reforming (also known as carbon dioxide reforming) is a method of producing synthesis gas (mixtures of hydrogen and carbon monoxide) from the reaction of carbon dioxide with hydrocarbons such as methane. Synthesis gas is conventionally produced via the steam reforming reaction. In recent years, increased concerns on the contribution of greenhouse gases (GHG) to global warming have increased interest in the replacement of steam as reactant with carbon dioxide.

[0004] The dry reforming reaction may be represented by: $CO_2 + CH_4 \rightarrow 2\,H_2 + 2\,CO$

[0005] Thus, two greenhouse gases are consumed and useful chemical building blocks, hydrogen and carbon monoxide, are produced. A challenge to the commercialization of this process is that the hydrogen that is produced tends to react with the carbon dioxide. For example, the following reaction typically proceeds with a lower activation energy than the dry reforming reaction itself: $CO_2 + H_2 \rightarrow H_2O + CO$.   Another challenge to commercialization is that dry reforming reaction is equilibrium limited which means that under most circumstances, the reaction does not go to completion.   Another challenge to commercialization is that the equilibrium extent of reaction is limited as the pressure increases. Gas Phase equilibrium reactions, such as the dry reforming reaction that have a net increase in moles of gas across the reaction are favored at lower pressure.   Operation at low pressure is disadvantageous due to the higher volume of reactor needed and the higher cost of compression to get the product gas prepared for subsequent use.

[0006]   As such, there is continuing interest and need to develop new methods and systems for more efficient dry reforming processes.

SUMMARY

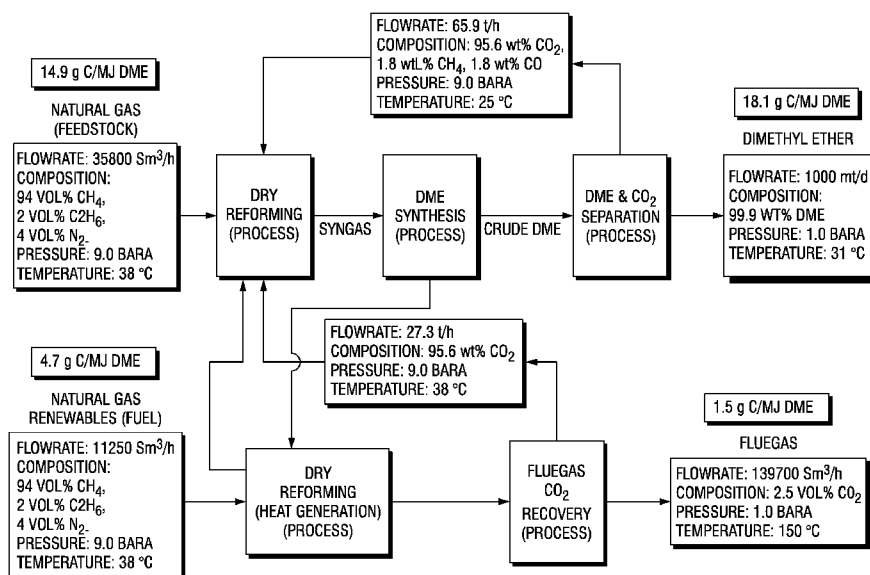[0007] Herein disclosed is a dry reforming reactor comprising a gas inlet near the bottom of the reactor; a gas outlet near the top of the reactor; a fluidized bed comprising a catalyst; and one or more hydrogen membranes comprising palladium (Pd). In an embodiment, the one or more hydrogen membranes comprises Pd alloy membranes, or Pd alloys supported on ceramic or metal substrates. In an embodiment, the one or more hydrogen membranes are placed vertically in the reactor as hydrogen membrane tubes hanging from the top of the reactor. In an embodiment, the hydrogen membranes are configured to selectively collect hydrogen from the tubes via one or more internal manifolds and sent to an external hydrogen collection system. In an embodiment, the membrane is coated with an erosion resistant layer.

[0008] In an embodiment, the gas inlet is configured to allow one or more feed streams to enter the reactor via a manifold or distributor. In an embodiment, the catalyst in the reactor comprises nickel and alumina. In an embodiment, the one or more feed streams fluidize the catalyst in the reactor. In an embodiment, the reactor is configured to allow reformed gas to exit the top of the reactor and separate from spent catalyst. In an embodiment, no steam or oxygen injection is needed for reactor.

[0009] In an embodiment, the reactor is operated at a pressure range of 500 to 900 kPa and a temperature range of 550 – 700 °C.

[0010] Herein also disclosed is a method of producing dimethyl ether (DME) comprising introducing one or more feed streams into a reformer to generate synthesis gas, wherein the reformer is a pressurized fluidized bed dry reforming reactor comprising a catalyst and a hydrogen membrane; and converting synthesis gas to DME.

[0011] In an embodiment, the hydrogen membrane removes hydrogen contained in the synthesis gas and shifts the equilibrium of the reforming reactions toward completion. In an embodiment, the hydrogen membrane comprises Pd alloy membranes, or Pd supported on ceramics or metals. In an embodiment, the hydrogen membrane is placed vertically in the reformer as hydrogen membrane tubes hanging from the top of the reformer. In an embodiment, hydrogen is collected from the hydrogen membrane tubes via one or more internal manifolds and sent to an external hydrogen collection system.

[0012] In an embodiment, the one or more feed streams enter the bottom of the reformer via a manifold or distributor. In an embodiment, the one or more feed streams fluidize the catalyst in the reformer. In an embodiment, the catalyst in the reactor comprises nickel and alumina. In an embodiment, reformed gas exits the top of the reformer and is separated from spent catalyst.

In an embodiment, spent catalyst is routed to a regenerator in which the catalyst is regenerated. In an embodiment, regenerated catalyst is returned to the reformer. In an embodiment, the reformer comprises a cyclone for solid gas separation.

[0013] In an embodiment, the reformer uses no process water and requires no oxygen. In an embodiment, the reformer is operated at a pressure range of 700-800 kPa and a temperature range of 600 – 700°C. In an embodiment, this process generates no greenhouse gas emissions. In an embodiment, wherein carbon dioxide recovered from the catalyst regenerator is used as feedstock in the reformer.

[0014] The foregoing has outlined rather broadly the features and technical advantages of the invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and the specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] For a detailed description of the preferred embodiments of the invention, reference will now be made to the accompanying drawings in which:

[0016] Figure 1 is a simplified block flow diagram illustrating the process for the production of DME from natural gas, according to an embodiment of this disclosure.

[0017] Figure 2 is a sketch illustrating the configuration of a reformer reactor, according to an embodiment of this disclosure.

[0018] Figure 3 is a diagram graph illustrating the ability to produce a 1:1 H_2:CO syngas at elevated pressure and reduced temperature in the reforming reactor, according to an embodiment of this disclosure.

[0019] Figure 4 shows an experimental set up of dry reforming, according to an embodiment of this disclosure.

[0020] Figure 5 illustrates an overall process flow sheet for process integration, according to an embodiment of this disclosure.

DETAILED DESCRIPTION

[0021] Herein disclosed is a dry reforming reactor comprising a gas inlet near the bottom of the reactor; a gas outlet near the top of the reactor; a fluidized bed comprising a catalyst; and one or more hydrogen membranes comprising palladium (Pd). In an embodiment, the one or more hydrogen membranes comprises Pd alloy membranes, or Pd alloys supported on ceramic or metal substrates. In an embodiment, the one or more hydrogen membranes are placed vertically in the reactor as hydrogen membrane tubes hanging from the top of the reactor. In an embodiment, the hydrogen membranes are configured to selectively collect hydrogen from the tubes via one or more internal manifolds and sent to an external hydrogen collection system.

[0022] In an embodiment, the gas inlet is configured to allow one or more feed streams to enter the reactor via a manifold or distributor. In an embodiment, the one or more feed streams fluidize the catalyst in the reactor. In an embodiment, the catalyst in the reactor comprises nickel and alumina. In an embodiment, the reactor is configured to allow reformed gas to exit the top of the reactor and separate from spent catalyst. In an embodiment, no steam or oxygen injection is needed for reactor.

[0023] In an embodiment, the reactor is operated at a pressure range of 700-800 kPa and a temperature range of $600 - 700°C$.

[0024] Herein also disclosed is a method of producing dimethyl ether (DME) comprising introducing one or more feed streams into a reformer to generate synthesis gas, wherein the reformer is a pressurized fluidized bed dry reforming reactor comprising a catalyst and a hydrogen membrane; and converting synthesis gas to DME.

[0025] In an embodiment, the hydrogen membrane removes hydrogen contained in the synthesis gas and shifts reforming reactions toward completion. In an embodiment, the hydrogen membrane comprises Pd alloy membranes, or Pd alloys supported on ceramic or metal substrates. In an embodiment, the hydrogen membrane is placed vertically in the reformer as hydrogen membrane tubes hanging from the top of the reformer. In an embodiment, hydrogen is collected from the hydrogen membrane tubes via one or more internal manifolds and sent to an external hydrogen collection system.

[0026] In an embodiment, the one or more feed streams enter the bottom of the reformer via a manifold or distributor. In an embodiment, the one or more feed streams fluidize the catalyst in the reformer. In an embodiment, reformed gas exits the top of the reformer and is separated from spent catalyst. In an embodiment, spent catalyst is routed to a regenerator in which the

catalyst is regenerated. In an embodiment, regenerated catalyst is returned to the reformer. In an embodiment, the reformer comprises a cyclone for solid gas separation.

[0027] In an embodiment, the reformer uses no process water and requires no oxygen. In an embodiment, the reformer is operated at a pressure range of 700-800 kPa and a temperature range of 600-700°C. In an embodiment, this process generates no greenhouse gas emissions. In an embodiment, wherein carbon dioxide recovered from the catalyst regenerator is used as feedstock in the reformer.

[0028] A pressurized fluidized bed (dry) reforming reactor utilizing Pd alloy membranes inserted into the fluidized bed for the purpose of permeating H_2 generated in the dry reforming reaction. A hydrocarbon feed stream, containing or co-fed with carbon dioxide, is fed and distributed into the base of the fluidized bed reformer, via a manifold or distributor. The reformer vessel is partially filled with a nickel based catalyst, suitable for dry reforming operating conditions. Reformed gas exits the top of the fluidized bed reformer, where it is separated from the catalyst. Spent catalyst is routed to a regenerator, where the catalyst is regenerated in an oxidizing environment. The regenerated catalyst is returned to the Reformer. H_2 produced in the reformer is extracted from the reformer fluidized bed, via multiple vertically oriented palladium alloy supported porous steel tubes, essentially 100% selective to H_2, located within the fluidized bed. The permeated H_2 is collected from the multiple membrane tubes via internal manifold(s), which route the H_2 to an external collection system.

[0029] As H_2 is permeated from the fluidized bed reformer, the dry reforming equilibria is shifted such that dry reforming reactions can proceed more or less to completion. The H_2 permeation facilitates the high degree of dry reforming, without the use of any steam injection into the reformer, at lower reforming temperatures and higher pressures than without the H_2 membranes.

[0030] Fluidized bed membrane reactors for the purpose of allowing dry reforming reactions to be conducted at higher pressure, lower reaction temperature and without any steam injection have not been disclosed in the art. In various embodiments, such higher pressure refers to pressures above atmospheric pressure and more specifically at pressures above 600 kPa; lower reaction temperature refers to temperatures less than 800°C. The forward equilibrium is favored at temperature above 800°C.

[0031] The overall chemical reaction for the process envisaged for the production of Dimethyl Ether (DME) (C_2H_6O) from dry reforming of methane and carbon dioxide is: $3\ CH_4 + CO_2 = 2\ C_2H_6O$.

[0032] In this process, carbon dioxide is consumed and converted into a useful product DME that can be used as a transportation fuel including as a replacement for diesel.

[0033] The dry reforming step uses a fluidized bed reactor with a Ni catalyst to convert methane to syngas. $CH_4 + CO_2 = H_2 + CO$

[0034] It is generally not easy to get to a H_2 to CO ratio of 1 in the product in practice. Catalysts often coke, deactivate, or are limited in the conversion of methane and result in a lower H_2 to CO ratio than desired.

[0035] The syngas to DME reaction can be written as: $6\ H_2 + 6\ CO = 2\ C_2H_6O$ (DME) + 2 CO_2

[0036] In some cases, the fluidized bed dry reforming reactor also contains a hydrogen membrane to preferentially remove hydrogen produced and force the reaction toward full conversion of the CO_2 and methane.

[0037] This dry reforming process is superior to other routes for the production of DME. It uses less natural gas than competing processes, uses no process water, and requires no oxygen plant, and has significantly lower greenhouse gas (GHG) emissions than the competing processes for DME production.

[0038] Figure 1 shows a simplified block flow diagram for this process. Figure 1 also illustrates flows and balances for a commercial process for the production of DME from natural gas.

[0039] Dry reforming. A pressurized fluidized bed (dry) reforming reactor utilizing Pd alloy membranes, or Pd alloy membranes supported on ceramic or other metal substrates inserted into the fluidized bed for the purpose of permeating H_2 generated in the dry reforming reaction. A hydrocarbon feed stream, containing carbon dioxide or co-fed with carbon dioxide, is fed and distributed into the base of the fluidized bed reformer, via a manifold or distributor. The reformer vessel is partially filled with a nickel based catalyst, suitable for dry reforming operating conditions.

[0040] Reformed gas exits the top of the fluidized bed reformer, where it is separated from the catalyst. Spent catalyst is routed to a regenerator, where the catalyst is regenerated in an oxidizing environment. The regenerated catalyst is returned to the Reformer. In an embodiment, hydrogen produced in the reformer is extracted from the reformer fluidized bed,

via multiple vertically oriented palladium alloy supported on porous steel tubes or ceramic substrates or other metallic substrates, essentially 100% selective to H_2, located within the fluidized bed. The permeated H_2 is collected from the multiple membrane tubes via internal manifold(s), which route the H_2 to an external collection system.

[0041] As H_2 is permeated from the fluidized bed reformer, the dry reforming equilibria is shifted such that dry reforming reactions can proceed to completion. The H_2 permeation facilitates the high degree of dry reforming, without the use of any steam injection into the reformer, at lower reforming temperatures and higher pressures than without the H_2 membranes.

[0042] Reformer / reforming reactor / reformer reactor. In an embodiment, Figure 2 shows the configuration of the reformer reactor. The reformer operates at approximately 700°C at a pressure of 700 – 800 kPa. Catalyst is fluidized by the incoming methane (or other hydrocarbon) and carbon dioxide feed. The feed gas passes through a gas distributor. The catalyst-gas mixture is in a fluidized bed. Inside the fluidized bed the hydrogen membranes tubes are placed hanging from the top of the reformer. The methane and carbon dioxide are reacted over the fluidized catalyst. The reaction will cause the formation of hydrogen and carbon monoxide via the dry reforming reaction.

[0043] In an embodiment, hydrogen will permeate through the membranes and be collected as hydrogen product leaving the reactor. The methane and carbon dioxide will continue to react as some of the hydrogen permeates away producing more hydrogen and carbon monoxide.

[0044] In some embodiments, the reformer has a top section that contains a cyclone for solid gas separation. Some amount of catalyst will continue to be transported toward the top of the reactor. The gas/catalyst mixture will enter the cyclone and the solid catalyst particles will separate from the gas and fall back toward the bottom of the reactor. The gas produced leaves the top of the reformer. Catalyst also leaves the reformer through an exit and the catalyst will then proceed to the regenerator. Regenerated catalyst enters the reformer catalyst bed as hot catalyst that supplies heat to the reformer. The catalyst will enter at approximately 900- 1000 °C. The catalyst residence time in the reformer is in the range of 0.5 – 4 minutes. The fluidized bed is preferentially operated in turbulent regime. The gas superficial velocity is in the range of 1 – 3 m/s.

[0045] The Nickel catalyst in the reformer with a mean particle size of approximately 200 microns and a nickel content of 2- 6 wt% on an alpha alumina support. For use in the system, the catalyst must be fluidizable, generically spherical, and must be attrition resistant during

operation. Suitable nickel alumina catalyst is disclosed, for example, in international patent application number PCT/US2005/036588, which is hereby incorporated herein in its entirety for all purposes not contrary to this disclosure and suitable nickel catalyst is disclosed, for example, in U.S. Patent 7,915,196 hereby incorporated herein in its entirety for all purposes not contrary to this disclosure.

[0046] Hydrogen Membranes. The addition of the hydrogen membranes to the reformer is optional but preferred. H_2 produced in the reformer is extracted from the reformer fluidized bed, via multiple vertically oriented palladium alloy supported on a porous ceramic substrate, essentially 100% selective to H_2, located within the fluidized bed. The permeated H_2 is collected from the multiple membrane tubes via internal manifold(s), which route the H_2 to an external collection system.

[0047] As H_2 is permeated from the fluidized bed reformer (the fuel reactor), the dry reforming equilibria is shifted such that dry reforming reactions can proceed more or less to completion. The H_2 permeation facilitates a higher degree of dry reforming, without the use of any steam injection into the reformer, at lower reforming temperatures and higher pressures than without the H_2 membranes. Figure 3 is a diagram illustrating the ability to produce a 1:1 H_2:CO syngas at elevated pressure and reduced temperature in the reforming reactor. Figure 4 shows an experimental set up of dry reforming.

[0048] Metallic membranes or metal coated ceramic supported membranes are hung inside the dual fluidized bed reactor, such as Pd or Pd alloy coated cylindrical structures hung inside the fluidized bed reactor or any other suitable structures. Palladium (Pd) based membranes have high hydrogen permeability and an almost infinite selectivity to hydrogen. A thin coating of Pd or Pd alloy 2 – 50 microns thick (with the minimal thickness being preferred for permeation but slightly thicker membranes desired for long term stability of the membrane) is deposited on the cylindrical support material. Ag, Pt, Au, Rh, Ru, and Pb additives have been added to the Pd to form alloys and improve hydrogen permeability. Self-supporting tubular hydrogen membranes have been successfully scaled up and are also contemplated for use in this catalytic membrane reactor/reformer.

[0049] The permeation rate through the hydrogen membranes varies significantly. The hydrogen permeation flux rates can vary from 10 -300 NM3 H2/hr/m2 of membrane area with the preferred range of 40-80 NM3 H2/hr/m2. The permeate pressure is relatively low at sub-atmospheric pressure (as low as 1 psia or approximately 7 kPa). The proper choice of the

balance between membrane surface area, hydrogen permeation, and overall reactor performance dictate the exact configuration of the reactor/reformer system.

[0050] The hydrogen product that goes to the manifold is then compressed and blended back with the reformer product gas to produce a combined syngas with a 1:1 hydrogen to carbon monoxide ratio. In some cases, sweep gas on the permeate side of the membrane is used to increase the flux at a higher pressure and reduce compression costs. If sweep gas is needed or desired, syngas or reformer product gas is used as the sweep gas.

[0051] Regenerator. Catalyst from the reformer is sent to the regenerator. The catalyst in the reformer can become deactivated by contaminants or by carbon deposited on the catalyst during the dry reforming reaction. Carbon formation during dry reforming reaction is one of the common problems with dry reforming process that uses a fixed bed. One of the advantages of using a fluidized bed reactor is that the catalyst can be regenerated frequently in air.

[0052] In an embodiment, the regenerator operates at approximately 900 - 1000 °C and catalyst is fluidized by air supplied by an air blower or other means at the bottom of the regenerator. Any carbon on the catalyst is burned off in the regenerator. In one embodiment, the regenerator is a fast fluidized bed where the air and catalyst are mixed at the bottom of the regenerator and the catalyst is conveyed to the top of the regenerator where the catalyst and flue gas are separated out. The superficial gas velocity in the regenerator dense bed is maintained at 1-3 m/s. The hot catalyst then recirculates to the entry nozzle on the reformer. In some embodiments, there is very little or no excess oxygen at the top of the regenerator.

[0053] In cases wherein carbon on the catalyst is not sufficient to keep the regenerator at the high temperature needed, supplemental fuel can be burned in the regenerator to heat the regenerator to operating temperature. In one embodiment, a mixer/burner is placed in the regenerator or adjacent to the regenerator vessel. Fuel and air are mixed and burned in the burner with the combustion product gases flowing into the regenerator and supplying any needed heat to the system. In an embodiment, methane is used as the supplemental fuel to the regenerator. In other embodiments, other fuels to the regenerator are used, such as renewable fuels including landfill gas, bio-ethanol, bio-digester gas, pyrolysis oils and liquid fuels, spent glycerol, biomass derived syngas. Alternatively, biomass is used in a biomass boiler where the hot flue gas from the boiler is used to heat the regenerator to operating temperature.

[0054] DME Production from Syngas. The hydrogen from the manifold is compressed and blended with the reformer product gas to produce a 1:1 H2/CO ratio syngas. The blended

syngas is compressed to approximately 5500 kPa. The blended syngas is reacted to produce primarily a Dimethyl Ether product by this reaction: $6\ H_2 + 6\ CO = 2\ C_2H_6O\ (DME) + 2\ CO_2$

[0055] In various embodiments, a single step is used to convert syngas to DME. There are multiple-step reactions that can also obtain DME as a product including a first step where syngas is converted to methanol and then methanol is dehydrated to DME. For one step synthesis, a bi-functional catalyst is used that does methanol synthesis and dehydration. There are a number of catalysts that can produce DME, such as mixtures of methanol catalyst (CuO/ZnO/Al2O3) with methanol dehydration catalysts (gamma-alumina). Other bifunctional catalysts such as Ni/Ce-ZrO2/Al2O3, CuO–ZnO–Al2O3 (CZA) over Clinoptilolite, CZA over various zeolites including ferrierite, ZrO2, ZSM-5, NaY or HY, are also used.

[0056] In an embodiment, slurry reactors and fixed bed reactors are used to produce DME from syngas. In an embodiment, a multi-tubular fixed bed reactor is used to produce DME from syngas to take advantage of the exothermic DME reaction and to better control reactor temperature and avoid hot spots.

[0057] In an embodiment, the conversion reactor has individual tubes of 20 – 30 mm in diameter filled with catalyst pellets. Syngas passes through the tubes and react to produce DME. In some embodiments, the reactor tubes are placed inside a shell. In some cases, inside the shell and around the tubes, water is circulated to regulate reactor temperature. Through the heat release in the reactor tubes, steam is generated in the shell.

[0058] In further embodiments, DME product is recovered from the outlet of the multi-tubular reactor and separated as product. CO_2 byproduct, produced in the DME synthesis loop, is separated for recycle to the dry reformer, via conventional distillation. The additional CO_2 required to satisfy the dry reforming stoichiometry is recovered from the pressurized regenerator flue gas, using an amine unit with a solvent such as methyldiethanolamine (MDEA). The CO_2 is then recycled as feed to the dry reforming reactor.

[0059] Process integration. In an embodiment as shown in Figure 5, the process as described herein is integrated for commercial application. The components in Figure 5 are explained in Table 1. Other alternative and equivalent arrangements are also possible, which are considered to be within the scope of this disclosure.

Table 1

10	Fluidizing nitrogen

12	Hydrogen
14	Natural gas feedstock
16	External fluegas
18	Natural gas knockout drum
20	Hydrodesulfurizer feed/effluent exchanger
22	Hydrodesulfurizer feed preheater
28	Hydrodesulfurizer vessel
30	CO2 plus loop purge
32	Natural gas fuel
34	Natural gas plus CO2 feed
36	Reformer
38	Recycle gas
40	Hydrogen
42	Hydrogen compressor
42	Reactor effluent
44	Recycle compressor
46	Synthesis gas knockout drum
48	Process condensate
50	Air compressor
52	Synthesis gas compressor
54	Synthesis gas
56	Converter (DME Reactor)
58	Converter Steam Drum
60	Circulator
62	Hydrogen permeate
64	Fuelgas
66	Loop Purge Recycle
68	Dimethyl ether (DME)
70	DME Column
72	CO2 Column
74	CO2 Compressor
76	Expander

78	Methanol Column
80	Methanol
82	Fusel oil
88	Wastewater
90	Amine Regenerator
92	Amine Pump
94	CO2 Absorber
96	Fluegas Compressor

Table 2

Parameter	Units	Proposed Dry Reforming Scheme	Alternate Tri-Reforming Scheme (KOGAS)	Alternate Tri-Reforming Scheme (JFE)
Natural Gas Consumption (incl. fuel)	MJ (LHV)/liter DME	25 – 27	26.9	27.6
Process Water Consumption	Liter H2O/liter DME	0	0.65	0.6
Oxygen Consumption	Kg/ liter DME	0	0.69	0.67
GHG emissions	G CO2/liter DME	120- 172	267	272

[0060] Advantages. The process as described herein has many advantages over existing processes for the production of DME. This process has (1) lower natural gas consumption per liter of DME produced, (2) no process water consumption, (3) no oxygen consumption, and (4) lower greenhouse gas (GHG) emissions per liter of DME produced. The details of these advantages are shown in Table 2 as this process is compared with tri-reforming schemes.

[0061] In addition, in this process, the pressurized reformer and regenerator operation facilitates less costly CO_2 recovery from the regenerator flue gas. This CO_2 roughly balances the net CO_2 makeup requirement for the DME synthesis. Hence, the process, as described, does not generate GHG emissions.

[0062] The process, as described, is capable of generating a useful 1:1 H_2:CO syngas for 100% dry reforming, without the requirement for steam or oxygen injection (as such in bi- or tri-reforming). This syngas quality is then useful for downstream product synthesis, without the need for Water Gas Shift reaction or CO_2 removal. The syngas product is available at elevated pressure, which significantly reduces syngas compression horsepower.

[0063] The process is able to generate a usable syngas product stream (e.g. 1:1 H_2:CO ratio) by dry reforming at elevated pressure and reduced temperature, as compared to other processes. The reduced reformer temperature allows for a drastic reduction in the catalyst circulation in a dual fluidized bed reforming system where the heat for the reforming reactions is supplied by catalyst circulation from a regenerator.

[0064] H_2 permeable membrane employed in a fluidized bed reformer is able to facilitate 100% dry reforming of a carbonaceous feedstock at elevated pressure and reduced temperature, to produce a useful syngas product. In some embodiments, CO_2 recovered from the pressurized catalyst regenerator is used as feedstock in the reformer.

[0065] While preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, and so forth). Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, and the like.

[0066] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the preferred embodiments of the present invention. The disclosures of all patents,

patent applications, and publications cited herein are hereby incorporated by reference, to the extent they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A dry reforming reactor comprising

        a gas inlet near the bottom of the reactor;

        a gas outlet near the top of the reactor;

        a fluidized bed comprising a catalyst; and

        one or more hydrogen membranes comprising palladium (Pd).

2. The reactor of claim 1 wherein said one or more hydrogen membranes comprises Pd alloy membranes, or Pd alloys supported on ceramic or metal substrates.

3. The reactor of claim 1 wherein said one or more hydrogen membranes are placed vertically in the reactor as hydrogen membrane tubes hanging from the top of the reactor.

4. The reactor of claim 3 wherein the hydrogen membranes are configured to selectively collect hydrogen from the tubes via one or more internal manifolds and sent to an external hydrogen collection system.

5. The reactor of claim 1 wherein the gas inlet is configured to allow one or more feed streams to enter the reactor via a manifold or distributor.

6. The reactor of claim 1 wherein the catalyst comprises nickel and alumina.

7. The reactor of claim 1 wherein the reactor is configured to allow reformed gas to exit the top of the reactor and separate from spent catalyst.

8. The reactor of claim 1 wherein no steam or oxygen injection is needed.

9. The reactor of claim 1 is operated at a temperature range of 600- 700°C and a pressure range of 700-800 kPa.

10. A method of producing dimethyl ether (DME) comprising

introducing one or more feed streams into a reformer to generate synthesis gas, wherein said reformer is a pressurized fluidized bed dry reforming reactor comprising a catalyst and a hydrogen membrane; and

converting synthesis gas to DME.

11. The method of claim 10 wherein said hydrogen membrane removes hydrogen contained in the synthesis gas and shifts reforming reactions toward completion.

12. The method of claim 10 wherein said hydrogen membrane comprises Pd alloy membranes, or Pd alloys supported on ceramic or metal substrates.

13. The method of claim 10 wherein said hydrogen membrane is placed vertically in said reformer as hydrogen membrane tubes hanging from the top of the reformer.

14. The method of claim 10 wherein hydrogen is collected from the hydrogen membrane tubes via one or more internal manifolds and sent to an external hydrogen collection system.

15. The method of claim 10 wherein said one or more feed streams enter the bottom of the reformer via a manifold or distributor.

16. The method of claim 15 wherein said one or more feed streams fluidize the catalyst in the reformer.

17. The method of claim 10 wherein reformed gas exits the top of the reformer and is separated from spent catalyst.

18. The method of claim 17 wherein spent catalyst is routed to a regenerator in which the catalyst is regenerated.

19. The method of claim 18 wherein regenerated catalyst is returned to the reformer.

20. The method of claim 10 wherein the reformer comprises a cyclone for solid gas separation.

21. The method of claim 10 wherein said reformer uses no process water and requires no oxygen.

22. The method of claim 10 wherein the reformer is operated at a pressure range of 700-800 kPa and a temperature range of 600-700°C.

23. The method of claim 10 generating no greenhouse gas emissions.

24. The method of claim 10 wherein carbon dioxide recovered from the catalyst regenerator is used as a feedstock in the reformer.
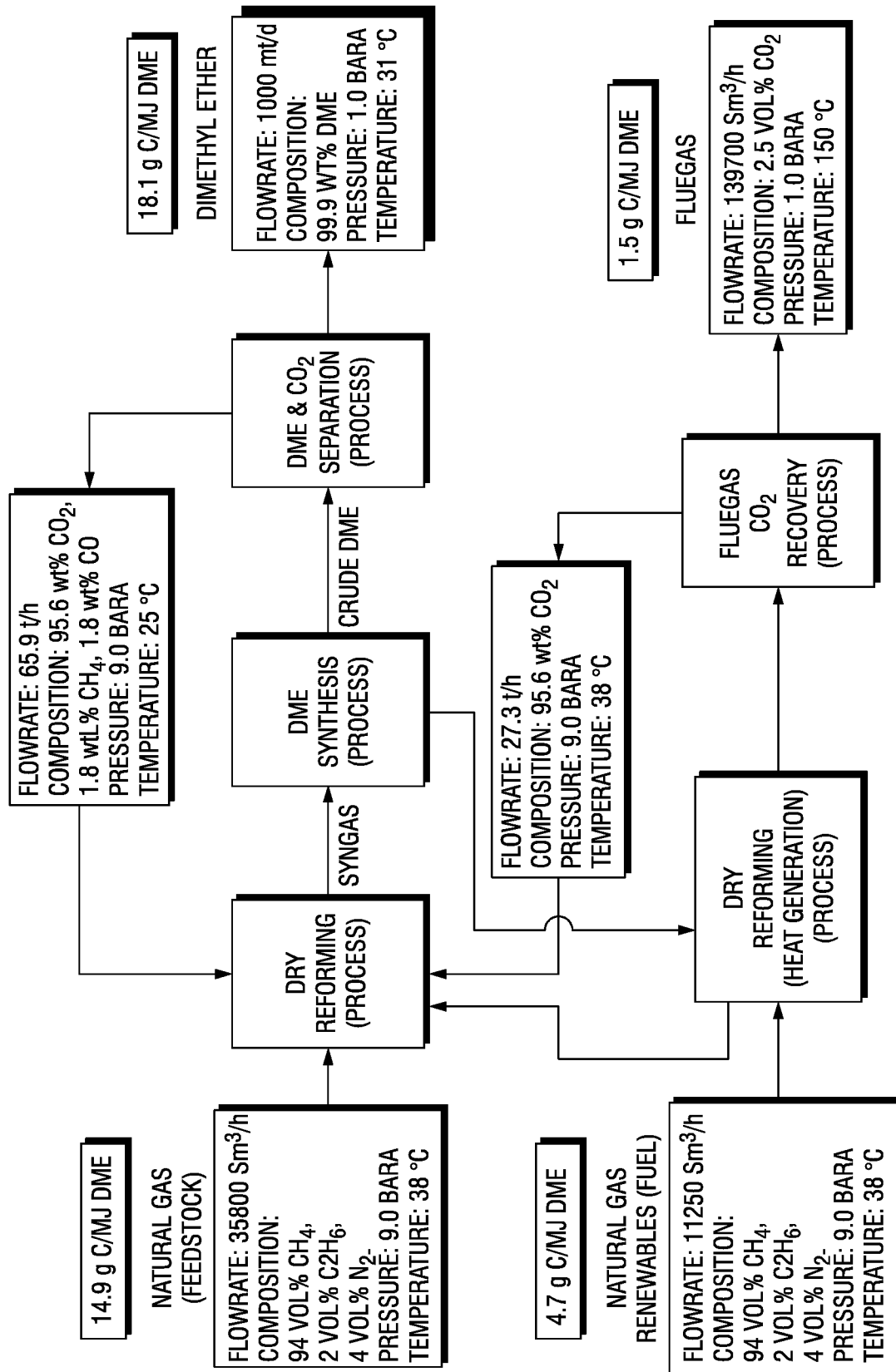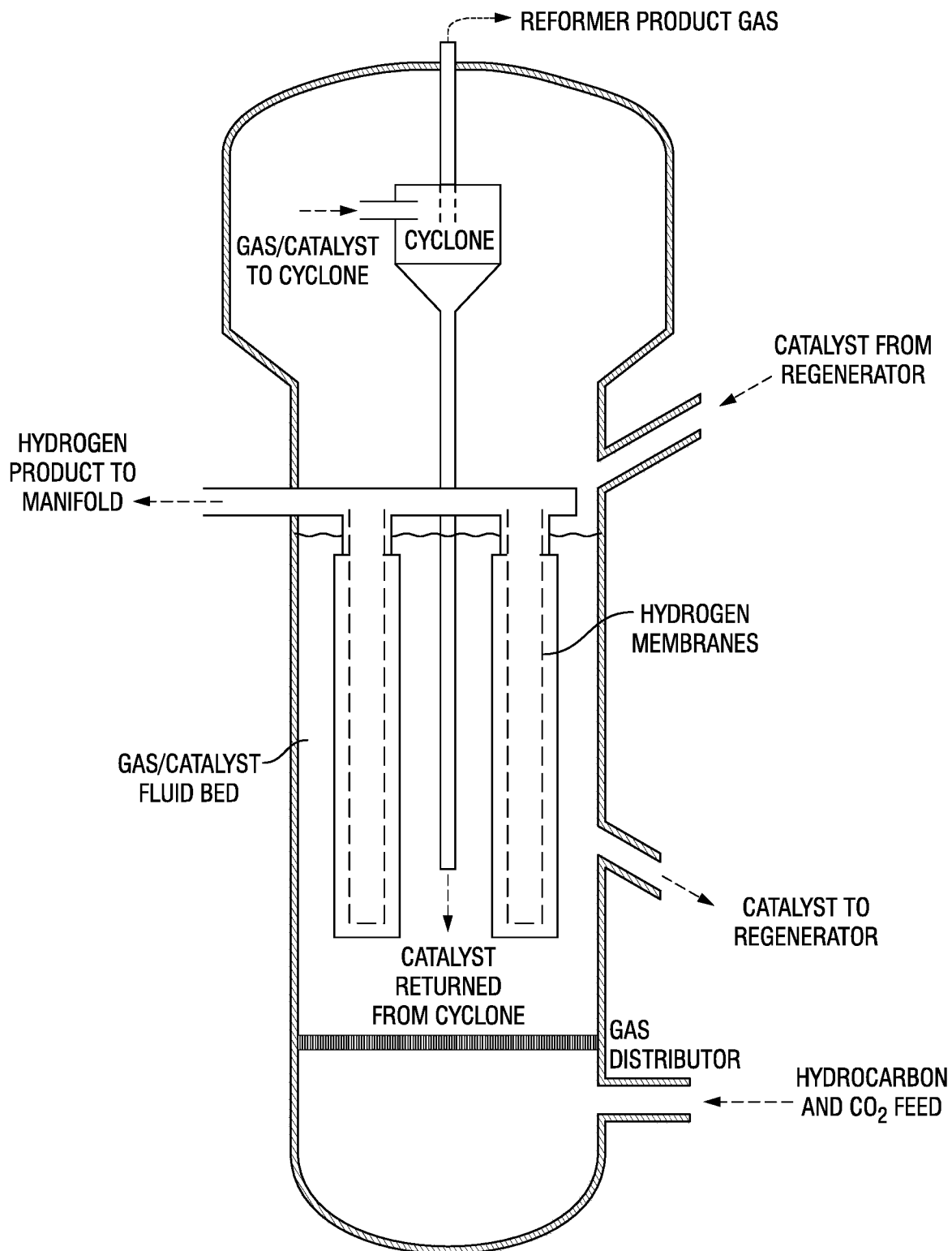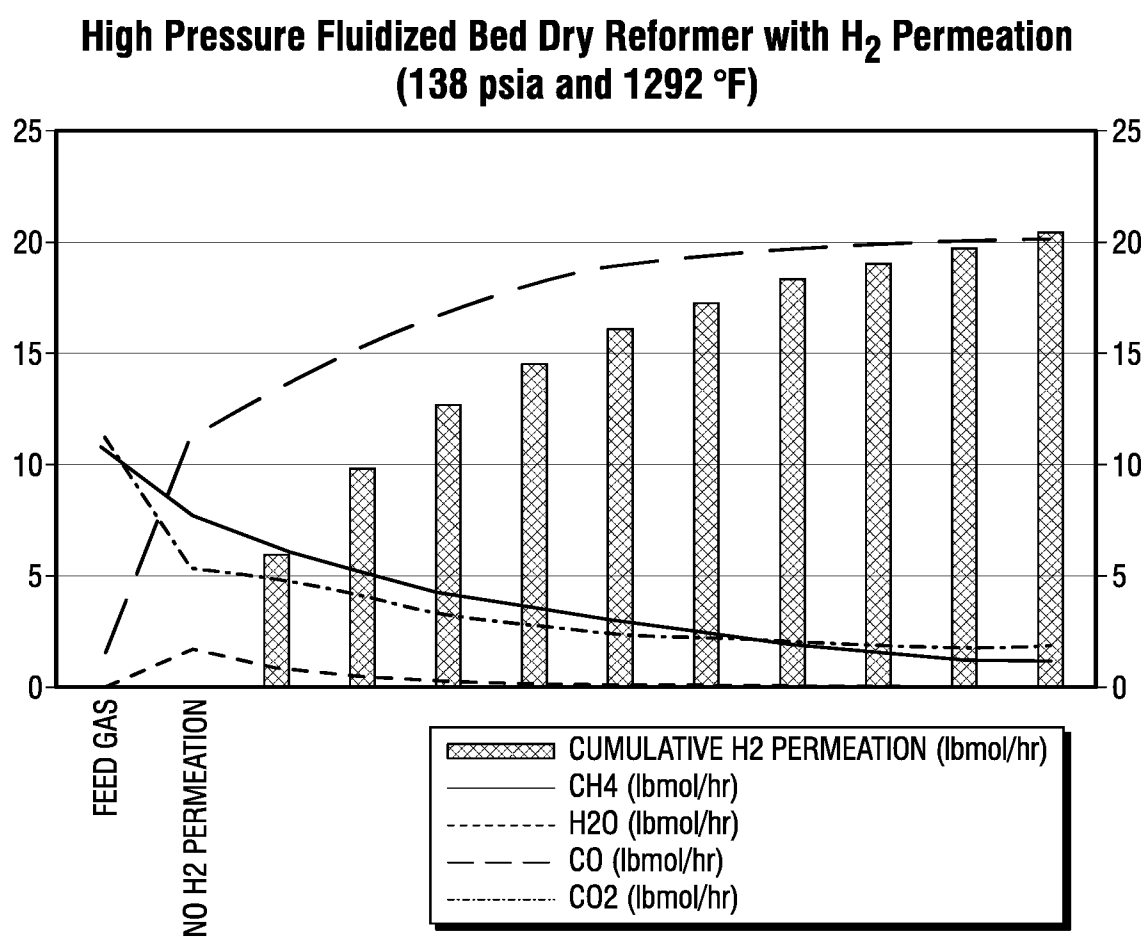
1/5

FIG. 1

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FIG. 2

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High Pressure Fluidized Bed Dry Reformer with H_2 Permeation
(138 psia and 1292 °F)

FIG. 3

SEC. AIR
NOZZLES

AIR

AIR

PRIM. AIR
NOZZLES

UPPER
LOOP SEAL

FUEL
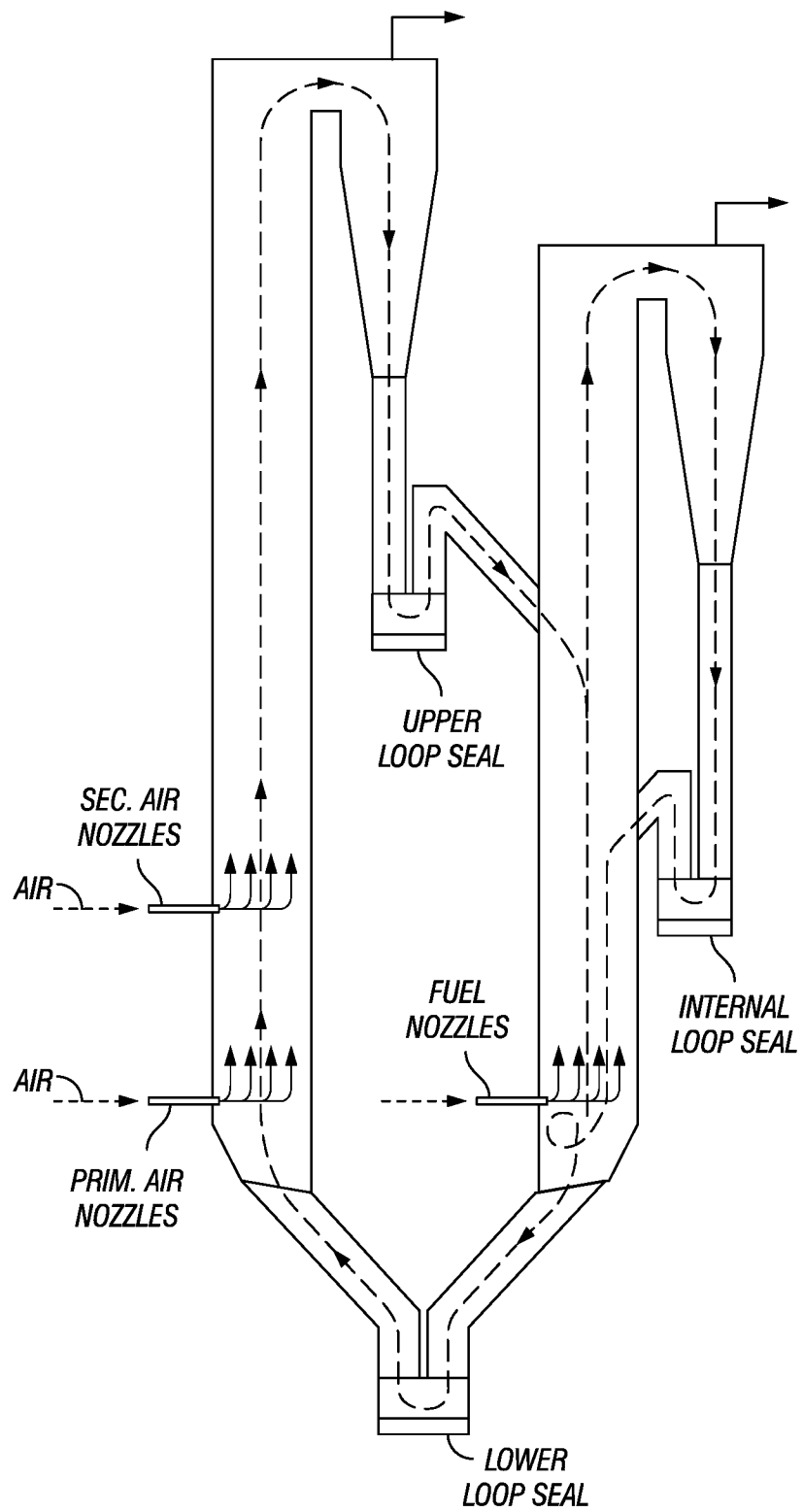NOZZLES

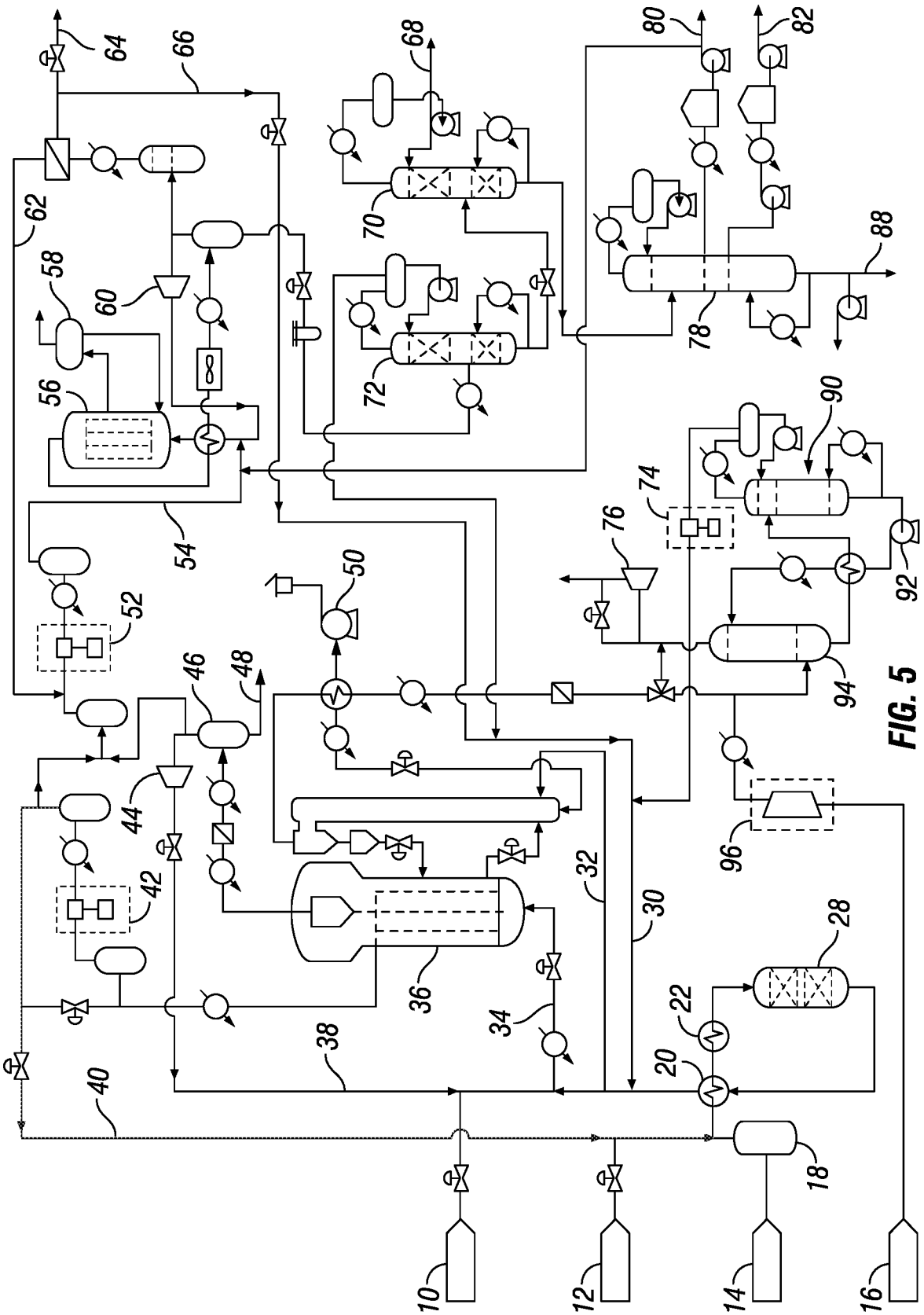INTERNAL
LOOP SEAL

LOWER
LOOP SEAL

FIG. 4

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FIG. 5

A. CLASSIFICATION OF SUBJECT MATTER

C10K 1/00(2006.01)i, B01J 19/24(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10K 1/00; C01B 3/26; C01B 31/20; H01M 8/06; B01J 29/70; C10G 3/00; B01J 23/755; B01J 7/00; B01J 19/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: dry reforming, hydrocarbon, methane, CO2 reforming, carbon dioxide, syn gas, hydrogen membrane, palladium, Pd alloy, fluidized bed, dluidized catalyst, nickel, alumina, converting, dimethyl ether, DME

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006-0013762 A1 (KUIPERS, JOHANNES ALFONSIUS MARIA et al.) 19 January 2006 See paragraphs [0027]-[0062]; claims 1-4 and 15-20; and figure 1.	1-24
Y	US 2003-0103893 A1 (DE LASA, HUGO IGNACIO et al.) 05 June 2003 See paragraphs [0041]-[0071]; claim 1; and figures 1 and 2.	1-24
Y	US 2015-0353840 A1 (ALLIANCE FOR SUSTAINABLE ENERGY, LLC.) 10 December 2015 See paragraphs [0008] and [0080]; and claim 15.	10-24
A	US 2011-0177410 A1 (ASSINK, GERRIT JAN BAREND et al.) 21 July 2011 See paragraphs [0026]-[0059]; and figure 1.	1-24
A	FRENI, S. et al., "Hydrogen production from methane through catalytic partial oxidation reactions," Journal of Power Sources, 2000, Vol. 87, No. 1, pages 28-38 See pages 28-35.	1-24

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 October 2017 (13.10.2017)	**13 October 2017 (13.10.2017)**

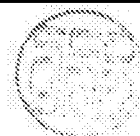| Name and mailing address of the ISA/KR	Authorized officer
International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea	LEE, Dong Wook
Facsimile No. +82-42-481-8578	Telephone No. +82-42-481-8163

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2003-0103893 A1	05/06/2003	CA 2364212 A1	03/06/2003
		US 6852668 B2	08/02/2005
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US 2011-0177410 A1	21/07/2011	EP 2035329 A2	18/03/2009
		US 8563185 B2	22/10/2013
		WO 2008-000782 A2	03/01/2008
		WO 2008-000782 A3	20/03/2008