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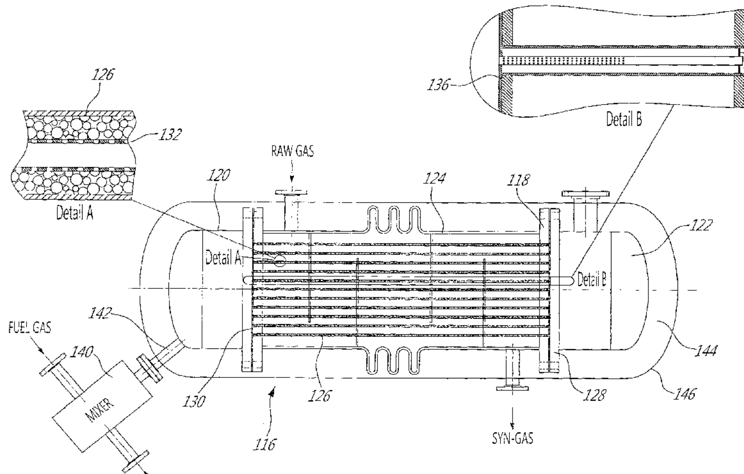

FIG. 4

(57) **Abstract**: The present application relates to a nanoparticle ceria based catalyst comprising CeO_2, at least one metal or metal oxide and at least one noble metal and the catalyst for use in a process and system for the production of hydrogen from raw gas. The application also relates to a reformer tube, a reformer, a water-gas shift reactor, a system and a process comprising a reformer, water-gas shift reactor and a separation step.

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SYSTEM AND PROCESS FOR THE PRODUCTION OF HYDROGEN FROM RAW GAS USING A NANOPARTICLE CERIA BASED CATALYST

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 61/289,049 filed December 22, 2009, the entire contents of which are hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present application generally relates to the process for the production of hydrogen from raw gas, as well as to a system for the production of hydrogen.

BACKGROUND ART

[0003] Across the western world the realization that cheap and abundant energy derived from fossil sources being coal, oil and natural gas to a lesser degree cannot be sustained going forward because of the ecological effect of climate change is taking hold. Green Energy defined as energy derived from renewable sources and energy autonomy is becoming extremely popular with small to medium size communities. Converting waste to electrical energy or energy carriers such as diesel or jet fuel is being implemented at an accelerated rate across Europe and North America. Incinerating municipal solid waste to produce electricity using the classic incinerator, boiler, steam turbine, and generator has been used worldwide for decades, however the low energy efficiency of that technological approach has created the need for innovation. The high energy efficiency of PEM fuel-cells and their present cost per kilowatt makes the small, independent, local production of electricity economically attractive if high purity hydrogen can be produced locally, economically and from a renewable source. The production of high purity hydrogen from locally generated waste gas or syn-gas using a process that combines raw-gas cleaning, steam reforming, water shift reaction and hydrogen separation provides a renewable source of hydrogen suitable for the local production of electricity for small communities, institutions, apartment buildings and commercial centers.

SUMMARY

[0004] In accordance with a first aspect of the invention, here is provided a nanoparticles ceria based catalyst comprising CeO_2, at least one metal, one metal oxide or a mixture thereof, and at least one noble metal. The metal or metal oxide is selected from the group consiting of Fe, Ti and Sn, and the noble metal is Pd and/or Pt.

[0005] In accordance with an aspect of the invention, here is provided a nanoparticles ceria based catalyst having the formula $Ce_{1-x}M_xPt/Pd_yO_{2-x}$ wherein M is Fe, Ti or Sn; x varies from 0.10 to 0.33, y varies from 0.01 to 0.03.

[0006] In accordance with another aspect of the invention, here is provided a tube for a reformer comprising an outer surface coated with a catalyst as defined above; a porous pipe at a first end thereof within the tube, the pipe defining an outer surface, a length and an inner passage capped at a second end opposite the first end, and an annular passage between the pipe and the tube.

[0007] In accordance with another aspect of the invention, here is provided a reformer comprising a

plurality of tubes, each of which comprises an outer surface coated with a catalyst as defined above; each of the tubes having a porous pipe at a first end thereof within the tube, the pipe defining an outer surface, a length and an inner passage capped at a second end opposite the first end; and an annular passage between the pipe and the tube; at least one inlet in communication with the reformer to introduce a raw gas to be reformed; and at least one reformed gas outlet in communication with the reformer to discharge a reformed gas to be produced.

[0008] In accordance with an aspect of the invention, here is provided a process for the production of hydrogen from a raw gas comprising the steps of a) providing a raw gas; b)introducing the raw gas into a reformer having a plurality of tubes, each of which comprises an outer surface coated with a catalyst as defined above and a flameless combustion within each of the tubes for heating the coated outer surface of each tubes; c) reforming the raw gas within the reformer by contacting the raw gas with the heated coated outer surface to promote a chemical reaction with the raw gas producing a reformed gas; d)reacting the reformed gas produced in c) in the presence of the catalyst as defined above in a single shift temperature step producing a mixture of hydrogen gas and carbon dioxide; and e) separating hydrogen from carbon dioxide produced in d).

[0009] In accordance with another aspect of the invention, the separation of hydrogen from carbon dioxide produced above comprises the steps of a) providing a mixture of hydrogen and carbon dioxide from which hydrogen will be separated; b)introducing the mixture of hydrogen and carbon dioxide in a vessel comprising an adsorption bed for adsorbing the carbon dioxide and allowing passage of hydrogen therethrough to a hydrogen accumulator;c)flushing the carbon dioxide containing an amount of hydrogen adsorbed on the adsorption bed within the vessel with carbon dioxide and transferring the carbon dioxide containing an amount of hydrogen with the mixture in a); d)removing the carbon dioxide within the vessel and transferring to the flameless combustion; and e)repressurizing the vessel and repeating steps b) to d).

[0010] In accordance with another aspect of the invention, here is provided a system for the production of hydrogen from a raw gas comprising a raw gas source; a reformer including an inlet in communication with the raw gas source for receiving the raw gas; a plurality of tubes, each of which comprises an outer surface coated with a catalyst as defined above to promote a chemical reaction with the raw gas for producing a reformed gas; and an outlet for discharging the reformed gas produced; a water-gas shift reactor including an inlet in communication with the outlet of the reformer for receiving the reformed gas; the catalyst for reacting the reformed gas into a mixture of hydrogen and carbon dioxide in one single shift temperature reaction step; and an outlet for discharging the mixture hydrogen and carbon dioxide; and a separation system for the separation of the hydrogen from the carbon dioxide including an inlet in communication with the water shift reactor outlet for receiving the mixture of hydrogen and carbon dioxide; an outlet for discharging the hydrogen; and an outlet for discharging the carbon dioxide.

[0011] In accordance with another aspect of the invention, here is provided a water-gas shift reactor comprising: a vessel having at least one inlet and at least one outlet; a packed bed within the vessel; a catalyst as defined above located within the packed bed suitable for reacting in a single shift temperature reaction step a reformed gas into a mixture of hydrogen and carbon dioxide; the at least one inlet is in communication with the vessel for receiving the reformed gas; and the at least one outlet in communication with the vessel for discharging the mixture of hydrogen and carbon dioxide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is flow diagram of a system for cleaning a raw gas in accordance with an embodiment of the present invention;

[0013] Fig. 2 is a detailed flow diagram of a system for the production of hydrogen from raw gas in accordance with an embodiment of the present invention;

[0014] Fig. 3 is a detailed flow diagram of a hydrogen purification system of the system of Fig. 2 in accordance with an embodiment of the present invention;

[0015] Fig. 4 is a is detailed view of a reformer of the system of Fig.2 in accordance with an embodiment of the present invention;

[0016] Fig. 5 represents the rate of conversion of CO to hydrogen as a function of temperature (°C) in a water-gas shift reaction in presence of a catalyst in accordance with an embodiment of the present invention;

[0017] Fig. 6a represents the oxidation of CO in presence of hydrogen as a function of temperature (°C) with a catalyst in accordance with an embodiment of the present invention;

[0018] Fig. 6b represents a preferential oxidation reaction (PROX reaction) of CO as a function of temperature (°C) with a catalyst in accordance with an embodiment of the present invention; and

[0019] Fig. 7 represents a ceramic honeycomb (a) without coating and (b) coated with a water-gas shift catalyst.

DETAILED DESCRIPTION OF PARTICULAR EMBODIMENTS

[0020] According to a general aspect of the claimed invention, the present disclosure relates to a process and a system for the production of hydrogen from raw gas. More specifically, the present disclosure provides a process and a system for reforming a raw gas into a reformed gas or syn-gas, converting the reformed gas into hydrogen and carbon dioxide by water-gas shift reaction and separating/purifying the hydrogen produced into high purity hydrogen suitable for use in, but not limited to, PEM fuel-cells. The raw gas may also be cleaned prior to be reformed.

[0021] In systems known in the art, hydrogen is produced in large quantities as a waste gas from the production of medium to large quantities of chloro-alkali plants, through natural gas steam reforming and in small quantities using electrolysis. None of the known systems with the exception of electrolysis when the electricity used is produced from a renewable source are using renewable feedstock and or energy source. The complete cycle energy efficiency of hydrogen production made according to the process and/or system in accordance with the claimed invention compares itself very favorably with hydrogen produced by electrolysis.

[0022] The term "raw gas" when used herein will be understood to refer to any waste gases from various sources such as landfills, anaerobic digesters, industrial, chemical and petrochemical process waste gas and solid waste gasifier syn-gas containing methane and hydrocarbons. It may also comprise raw gases that have been cleaned by any processes known in the art.

[0023] Reference will now be made to the embodiment illustrated in the drawings and described herein. It is understood that no limitation of the scope of the disclosure is thereby intended. It is further understood that the present disclosure includes any alterations and modifications to the illustrated embodiments and includes further applications of the principles of the disclosure as would normally occur to one skilled in the art to which this disclosure pertains.

[0024] Referring to Fig. 1, the raw gas cleaning system (10) in accordance with the invention is shown. The raw gas cleaning system (10) is designed to accept any kind of raw gas as long as that gas contains methane and/or hydrocarbons. However, the raw gas may also contain several impurities that is detrimental to the continuous performance of the catalyst and must be removed from the raw gas prior to the conversion thereof into reformed gas or syn-gas and eventually in hydrogen. The main impurities that must be removed from the raw gas include but not limited to water, sulfur, chlorinated compounds, siloxanes, halogens or combinations thereof.

[0025] The raw gas cleaning system (10) which may eventually constitute a first part of the system in accordance with the invention is configured to substantially remove impurities from the raw gas. The cleaning system (10) includes the following components as illustrated on figure 1: a raw gas cooling stage, a sulfur removal stage, a thermal swing adsorption stage, and a final gas filtration stage.

[0026] The raw gas is drawn from a raw gas source and fed by a rotary centrifugal gas blower (32), into a knock-out vessel (12) containing a mist arrestor (14) then into a gas cooling unit (16) which brings the temperature of the raw gas to 5°C. Two methods, which are known in the art, may be used to achieve the cooling of the raw gas: indirect cooling by using a chilled water heat exchanger/condenser or direct cooling by using a chilled water scrubber wherein the raw waste gas is contacted with a cold water spray and cooled to 5°C. In both cases the amount of water contained in the raw gas is reduced to the water content of the saturated gas at 5°C, the excess water is condensed out. As water is condensed, a certain amount of condensable hydrocarbons, siloxanes and hydrogen sulfide is condensed and removed from the raw gas with the water condensate.

[0027] In the cleaning system (10) of fig. 1, a direct gas cooling system is shown, the cooling vessel (16) is cylindrical, up-flow and has a diameter calculated to provide with a gas velocity of approximately 1.5 to 2 meters per second. The vessel bottom part acts as a reservoir for the cooling water and his level is controlled by a level control valve which feeds demineralized water as make-up water.

[0028] Above the gas entry port, a high exchange surface packing bed (20) is installed. The height of this packing is for example 1 to 2 meters allowing for a 1 to 2 seconds contact time. Above the packing bed, a cold water header and spray nozzle (22) provide for full flooding of the packing to achieve the required thermal exchange between the gas and the water in order to cool the gas to the required temperature of 5°C. Above the cold water spray system a mist eliminator (18) removes the water droplets entrained in the gas stream prior to the exit of that cooled gas at the top of the vessel. The cooling water circuit is composed of a water pump (28) an air cooled chiller (30), a liquid to liquid heat exchanger (26) and connection piping (24).

[0029] The cold (5°C) raw gas is passed through a hydrogen sulfide removal vessel (36) containing a bed of activated carbon (38). The diameter of the hydrogen sulfide removal vessel is calculated to obtain a gas velocity through an activated carbon bed of for example between 0.5 meter/second and 1.0 meter per second. The height of the bed is for example between 1.0 meter and 2.0 meters, depending on the raw gas contamination level, to provide a minimum of 3 to 6 months activated carbon bed life.

[0030] In a preferred embodiment, two vessels are installed in parallel to provide uninterrupted cleaning of the raw gas. The activated carbon used is washable and a carbon bed wash system is implemented including water piping (50), a on/off solenoid valve (48) to activate and stop the carbon bed washing, a water header (46) and a water spray nozzle (44). The percolate from the carbon bed washing operation is trickled to the bottom of the vessel and is discharged to the drain system through drain nozzle (42) connected to the drainage piping (34).

[0031] The gas is then passed through a Thermal Swing Adsorption (TSA) unit wherein the remaining siloxanes, chlorinated hydrocarbons and halogens are removed. In Fig.1, the TSA unit consist of two vessels (52) and (54), each containing a mixture of absorbent materials (56) and (58). The mixture of absorbent materials contains for example 10% of silica gel coated alumina and 90% of reactive activated carbon.

[0032] In one embodiment, the gas is passed through both vessels arranged in a parallel configuration, valve (60), (68), (64) and valve (72) are opened and all other valves (62), (66), (70) and (74) are closed. After an extended period of time of about five days but before the saturation of the mixture of absorbent materials, one of the two vessels is isolated by closing valves (60) and (64) then readied for thermal regeneration by opening valves (62) and (66).

[0033] During the regeneration cycle only one of the two vessels is in absorbing mode and the gas velocities values through that vessel are doubled compared to normal value. Pressure drop calculations and actual field tests have demonstrated that this practice is not detrimental to the expected life time of the mixture of absorbent materials as the duration of the regeneration phase is not long, lasting less than 24 hours for example to regenerate the two vessels.

[0034] The absorbent bed is regenerated by heating the bed to a temperature of about 350°C and venting the desorbed vapors to a reformer heater/combustor where these desorbed gases are combusted along with supplementary fuel. The heating and desorption of the vessel under desorption mode is provided by air pressurized by a centrifugal blower (78) then heated by an electric heater (76).

[0035] During the desorption mode of vessel (52) valves (62) and (66) are open and valves (60) and (64) are closed. The desorption of one vessel occurs while the other vessel is in the adsorption mode, allowing for continuous production of clean gas. After complete desorption of the absorbent bed in vessel (52) the electric heater (76) is turned off and vessel and absorbent bed is cooled by fresh air. Once the temperature of the absorbent bed in vessel (56) is back to ambient temperature the vessel and the absorbent bed is purged by nitrogen stored under pressure in cylinders (40).

[0036] During cooling of the adsorption bed and the nitrogen purge operation the exhausted gas is vented to atmosphere. Once the absorbent bed of vessel (52) is fully regenerated, that vessel is brought back on line by the closing of valves (62) and (66) and the opening, 5 seconds later, of valves (64) and (60) in that order. After one minute vessel (54) is brought to the regeneration mode by following the exact same procedure as previously followed by vessel (52). Valves (68) and (72) are closed then valves (70) and (74) are opened, electric heater (76) switched on and the full thermal desorption, venting, cooling, and nitrogen purging sequence is performed after which valves (70) and (74) are closed and valves (72) and (68) are opened in that sequence.

[0037] Once the thermal desorption sequence of both vessels (52) and (54) is completed, the fresh air blower (78) is stopped until the initiation of the next thermal desorption sequence. During the thermal desorption sequence, the desorbed gases is directed to the reformer combustor through piping (87).

[0038] At the discharge of the TSA unit the raw gas is cleaned to acceptable feedstock quality for catalytic reforming and contains for example less than 2 ppm of hydrogen sulfide, less than 1 ppm of chlorinated hydrocarbons and less than 50 to 100 ppb of halogens. The clean raw gas is filtered, to remove any airborne particulate, by passing through cartridge filter (80) then pumped to the reformer through piping (84) using the gas blower (82).

[0039] Turning to Fig. 2, a system (85) for producing hydrogen from a raw gas is described. The system (85) comprises a raw gas source (84); a reformer (116) including an inlet in communication with the raw gas source (84) for receiving the raw gas; a plurality of tubes, each of which comprises an outer surface coated with a ceria based catalyst to promote a chemical reaction with the raw gas for producing a reformed gas; and an outlet for discharging the reformed gas produced; a water-gas shift reactor (100) including an inlet in communication with the outlet of the reformer (116) for receiving the reformed gas; the catalyst for reacting the reformed gas into a mixture of hydrogen and carbon dioxide in one single shift temperature reaction step; and an outlet for discharging the mixture hydrogen and carbon dioxide; and a separation system (106) for the separation of the hydrogen from the carbon dioxide including an inlet in communication with the water shift reactor outlet for receiving the mixture of hydrogen and carbon dioxide; an outlet for discharging the hydrogen; and an outlet for discharging the carbon dioxide.

[0040] In systems known in the art, reforming consists in breaking bonds between carbon and hydrogen atoms of methane and hydrocarbon molecules contained in a raw gas and recombines in the presence of a catalyst with dissociated water molecules to produce carbon monoxide and hydrogen commonly defined as reformed gas or syn-gas. The steam reforming reactions are generally as follows:

$$Cn_1Hn_2 \rightarrow Cn_1 + Hn_2$$

$$n_1H_2O \rightarrow n_1H_2 + \frac{1}{2}\, n_1O_2$$

$$Cn_1 + Hn_2 + n_1H_2 + \frac{1}{2}\, n_1O_2 \leftrightarrow n_1CO + (\frac{1}{2}n_2 + n_1)H_2$$

[0041] Conventional SMR processes use a nickel catalyst and a reform temperature of between 850°C and 750°C below which the reform reaction stops. It is known that the reform reaction is endothermic, the temperature of the gas mixture decreases as the reform reaction progresses. If heat is not provided continuously to the gas mixture being reformed, the reaction will be incomplete.

[0042] To achieve a complete reform reaction and continuously provide heat to the raw gas, large conventional steam reformers consist essentially of externally heated tubes containing a nickel catalyst coated on a honeycomb ceramic substrate within the tube. The tubes are vertically mounted and the burners, installed at the top tube sheet of the reformer are projecting their flame downward between the reforming tubes. In this conventional design the reformer tubes are long, with nominal length in the 10 to 13 meter range.

[0043] Such design is not practical for small reformers such as the ones described in the present application. Reformers known in the art can process gas flows in the range of 40,000 kg/hr to 200,000 kg/hr. The reformers in accordance with the present application are, for example, in the range of 20 kg/hr to 5,000 kg/hr.

[0044] In an embodiment, the raw gas to be reformed is outside the tubes rather than inside the tubes and the catalyst is coated on an external surface of the tubes and the required heat input to keep the temperature of the raw gas to be reformed constant, is provided by a flameless combustion of combustion gas inside the tubes. Preferably, the flameless combustion derives from a combustion gas comprising a mixture of fuel gas and combustion air in presence of the catalyst. Since the reform reaction is endothermic and occurs only in a narrow temperature range of between about 750°C and about 850°C, the temperature of the surface of reforming tubes must be kept constant along the whole length of the tubes.

[0045] In an embodiment, the catalyst in accordance wit the invention comprises a nanoparticles ceria based catalyst comprising CeO_2, at least one metal, metal oxide or a mixture thereof, and at least one noble metal. Preferably, the metal or metal oxide is selected from the group consiting of Fe, Ti and Sn and the noble metal is Pd and/or Pt.

[0046] In a preferred embodiment, the nanoparticles ceria based catalyst has the formula $Ce_{1-x}M_xPt/Pd_yO_{2-x}$

wherein M is Fe, Ti or Sn; x varies from 0.10 to 0.33, y varies from 0.01 to 0.03.

[0047] Preferably, the catalyst has the formula $Ce_{1-x}Sn_xPt_yO_{2-x}$, wherein x and y are as defined above.

[0048] The structure of the CeO_2 is preferably a fluorite.

[0049] In one embodiment, the catalyst may be in the form of a solid solution of titanium oxide and cerium oxide where platinum ions for example have been substituted in the +2 state. In an alternative embodiment, the catalyst has the formula $Ti_{0.99}Pt_{0.01}O_{1.99}$. It was observed that $Ti_{0.99}Pt_{0.01}O_{1.99}$ exhibits a higher activity than the cerium oxide based or the mixture of titanium and cerium oxide catalyst. The platinum boosted titanium oxide catalyst was selected and tested for deactivation. There was no sintering of platinum nor any carbonate formation which indicates that the catalyst would not deactivate even after prolonged reaction.

[0050] In an embodiment, a reformer (116) in accordance with the invention is shown in Fig.2 and more specifically in Fig. 4. Referring to Fig.4, the reformer (116) consists in a flanged tube bundle (118) connected to one dish head at each end. One dish head (120) receives the fuel gas and combustion air and the dish head (122) at the other end of the tube bundle receives the combusted gases exiting from the discharge end of the tubes. Each of the reformer tubes (126) is for example welded at each end to the reformer tube bundle flanges (128) and (130) and has an inner tube or pipe (132) having for example pores to part of its length at a first end thereof within the tube (126), the pipe (132) defining an inner passage capped at a second end opposite the first end, and an annular passage between the pipe (132) and the tube (126). It is contemplated that each of the reformer tubes may be secured at each end to the reformer tube bundle flanges (128) and (130) by any suitable means known in the art.

[0051] Still referring to Fig. 4, a tube (126) for a reformer is shown in detail and comprises an outer surface coated with a catalyst; a porous pipe at a first end thereof within the tube (126), the pipe (132) defining an outer surface, a length and an inner passage capped at a second end opposite the first end, and an annular passage between the pipe and the tube.

[0052] The annular passage may be filled with the catalyst along the length of the tube (126) or alternatively, the porous pipe outer surface is coated with the catalyst (not shown).

[0053] In an embodiment, a reformer (116) comprises a plurality of tubes (126), each of which comprises an outer surface coated with a catalyst in accordance with an embodiment of the present invention; each of the tubes (126) having a porous pipe (132) at a first end thereof within the tube (126), the pipe (132) defining an outer surface, a length and an inner passage capped at a second end opposite the first end; and an annular passage between the pipe (132) and the tube (126); at least one inlet in communication with the reformer (116) to introduce a raw gas to be reformed; and at least one reformed gas outlet in communication with the reformer to discharge a reformed gas to be produced.

[0054] In an alternate embodiment (not shown), a space within the reformer between the outer surface of the plurality of tubes may be filled with the catalyst.

[0055] The term "porous" when used herein will be understood to refer to pores, perforations, holes, meshes, channel, or apertures. Their size, number and location along the length of the pipe are designed to provide a regular injection of combustion gas along the whole length of the reforming tubes to avoid hot and or cold points.

[0056] The reformer (116) has at least one inlet in communication with a raw gas source for introducing a raw gas; and at least one reformed gas outlet in communication with the reformer (116) for discharging a reformed gas to be produced.

[0057] The tube bundle (118) is placed inside a cylindrical outer shell (124) which is secured, for example welded, at each end to the flange of the tube bundle. As the outer shell (124) may be subjected to lower temperatures than the reformer tubes, the outer shell and reformer tubes may expand at different rates, to mitigate these different expansions and avoid undue stress on the reformer inner components, the outer shell may be fitted with welded bellows type expansion coils. This type of expansion compensation devices are common practice when processes operate at low pressure as is the case here.

[0058] Each reformer tube has an outside diameter between about 25 mm and about 100 mm, the inner tubes have an outside diameter between about 10 mm and about 70 mm, the wall thickness of the reformer tubes is, but not limited to 6 mm and the wall thickness of the inner tube is, but not limited to 2 to 3 mm. The tube may be of alloy steel or any other suitable material.

[0059] The pipes (132) are supported at the inlet end by and welded to a tube sheet (136) at the other end they are supported by a star type spacer (138) which allow for the lateral movement of the tube during thermal expansion and contraction as well as allow for the passage of the combustion gases. It is contemplated that the pipes (132) may be secured by any other suitable means known in the art without departing from the scope of the invention.

[0060] The reformer vessel and the internal parts may be manufactured from grade 310 stainless steel and higher alloys and are externally insulated (144) and cladded (146) to allow for the minimum heat loss and also for operator protection. The design of the reforming system is such that no exposed surface shall reach a temperature superior to 60°C. It is contemplated that the reformer (116) may be built from any adequate material known in the art. Those skilled in the art producing hydrogen will be able to select and built a reformer having the preferred characteristics herein described.

[0061] Referring to Fig.2, the raw gas (84) or alternatively, a clean raw gas from a gas cleaning system as shown in Fig.1, is mixed with vent gas from a VPSA hydrogen purification unit (114) and vent gas from the TSA unit of the raw gas cleaning system (86) in order to optimize the energy balance of the process and to provide extra heat capacity. This gas mixture is heated to a temperature of for example 250°C by passing through heat exchanger (96) and is introduced as fuel gas with the required combustion air into the gas mixer (140) then into the reformer inlet dish head (120) and then passed through the reformer pipes (132).

[0062] Atmospheric air is pressurized by a centrifugal blower (108) and is heated to approximately 250°C by passing through heat exchanger (102) and is mixed with the fuel gas in an inline kinetic gas mixer (140) installed upstream of the reformer inlet dish head inlet nozzle (142).

[0063] An air/fuel mix is controlled by modulating the flow of air through the inline kinetic gas mixer (140). This is done by adjusting the discharge pressure of the centrifugal blower (108) by modulating a pressure reducing valve (110). This adjustment of the air/fuel ratio is needed to achieve complete combustion of the fuel gas and the required wall temperature all along the reformer tubes length.

[0064] De-mineralized water is pumped by pump (88) and brought under pressure into a heat exchanger/boiler super-heater (90) where steam is generated at a temperature of about 200°C and a pressure of about 2.5 bars. Raw gas or clean raw gas is introduced into the steam piping through piping (84) and the mixture of raw gas and steam is directed through piping to heat exchanger (92) where the temperature of the gas mixture is raised to about 600°C. The hot gas mixture is introduced in the reformer (116) where it follows a five pass path from one end of the reformer (116) to the other end of the reformer (116) and is in contact with the heated catalyst coated external surface of the reformer tubes (126).

[0065] The gas at the inlet of the reformer is but not limited to a mixture of methane, volatile hydrocarbons, and water with some carbon dioxide and nitrogen. The reformed gas at the outlet of the reformer is but not limited to a mixture of carbon monoxide and hydrogen with some water, carbon dioxide, nitrogen and traces of methane and volatile hydrocarbons.

[0066] The temperature of the reformed gas at the discharge of the reformer is about 750°C. That temperature is reduced by passing the reformed gas through heat exchanger (92) where thermal energy is recovered and transferred to the raw-gas/steam mixture entering the reformer. At the outlet of heat exchanger (92) the reformed gas temperature is about 350°C. The reformed gas is further cooled to a temperature of about 275°C by passing through heat exchanger (96). Finally the reformed gas is cooled to about 250°C by passing through an air cooled heat exchanger (98) prior to its introduction into the water-gas shift reactor (100).

[0067] The water-gas shift reaction generally occurs first at high temperature (about 300°C to about 380°C) in a high temperature shift reactor then after some cooling of the gas is completed at a lower temperature (about 200°C to about 250°C) in a low temperature shift reactor. The catalyst used in the high temperature shift reactor is generally Fe_2O_3/Cr_2O_3 and the catalyst used in the low temperature shift reactor is generally $Cu/ZnO/Al_2O_3$. The water-gas shift reaction in presence of catalyst is as follows:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

[0068] In one embodiment, the catalyst in accordance with the invention is used for water-gas shift reaction. The catalyst which does not follow the Gibbs equilibrium curve, permits the water-gas reaction to be completed in a single shift temperature step rather than a high temperature followed by a low temperature step as usually seen in the art. Pilot testing of the catalyst in water-gas shift reaction conditions has demonstrated that a carbon monoxide concentration of less than about 0.9% is achieved in one single shift reaction step.

[0069] Since the catalyst in the water-gas shift reaction is to be loaded for example onto a ceramic honeycomb and to avoid handling the fine powder material, the method for coating the nano-crystalline material directly on the honeycomb is using the solution combustion method. The method involves dip-dry combustion process of the ceramic honeycomb. The catalyst mentioned above is coated to the extent of 2 to 3% of the weight of the honeycomb. The method is a batch process.

[0070] The rate of CO conversion as a function of temperature for the catalyst in the water-gas shift reaction was studied and the rate at 300^{0}C was 12 micromoles per gram per second. Figure 5 shows the variation of the rate of conversion as a function of temperature. At 300 ± 25 ^{0}C over 99.5% conversion of CO is achieved with the catalyst at 280^{0}C to 320^{0}C. The catalyst gave 100% hydrogen selectivity. Levels of impurities observed such as methane, methanol and aldehydes were below 2 ppm.

[0071] The catalyst may also be used in preferential oxidation (PROX reaction) of CO to remove residual CO. In Figure 6, CO oxidation in presence of excess hydrogen is shown. CO oxidation occurs at room temperature in the presence of the catalyst.

[0072] In Figure 7, ceramic honeycombs (a) without coating and (b) coated with a water-gas shift catalyst are shown.

[0073] In one embodiment, a water-gas shift reactor (100) in accordance with the invention is shown in Fig. 2. The shift reactor vessel (100) may be cylindrical with a diameter calculated to provide for a gas space velocity of for example 15,000 h^{-1}. The height of the shift reactor is calculated to provide the required catalyst surface area and residence time to complete the shift reaction of carbon monoxide and water into hydrogen and carbon dioxide. It is contemplated that the water-gas shift reactor (100) may be built from any adequate material known in the art.

[0074] The water-gas shift (100) reactor comprises a vessel having at least one inlet and at lest one outlet; a packed bed into the vessel; the catalyst as defined above located within the packed bed suitable for reacting in a single shift temperature reaction step a reformed gas into a mixture of hydrogen and carbon dioxide;the at least one inlet is in communication with the vessel for receiving the reformed gas; and the at least one outlet in communication with the vessel for discharging the mixture of hydrogen and carbon dioxide.

[0075] In one embodiment, the catalyst used in the water-gas shift reaction is coated and baked on a support coat (wash coat) itself coated on a ceramic honeycomb monolith. It is also contemplated that any suitable support known in the art may be used. The ceramic monolith substrate is a standard commercial product, available in blocks of various dimensions to accommodate cylindrical or rectangular section designs. The number of channels per square inch is usually 400. Each layer of monolith blocks is spaced to ensure that the gas can pass from one row of blocks to the next without undue pressure drop.

[0076] The water-gas shift reactor (100) vessel is constructed of 304 stainless steel and is externally insulated and cladded to allow for the minimum heat loss and also for operator protection. The design of the shift reaction system is such that no exposed surface shall reach a temperature superior to 60°C. Those skilled in the art producing hydrogen will be able to select and built a water-gas shift reactor having the preferred characteristics herein described.

[0077] Still referring to Fig. 2, the gas exiting from the water-gas shift reactor (100) is at a temperature of about 285°C which is not suitable for the separation stage of the process where hydrogen is purified to about 99.999%. To cool the gas that is coming from the water shift gas reactor, an air to gas heat exchanger is implemented. The hot gas from the shift reactor is cooled in heat exchanger (102) to a temperature of about 125°C by air coming from the combustion air blower (108) on its way to the combustion side of the reformer.

[0078] The separation of hydrogen from carbon dioxide and other gaseous impurities requires a temperature of less than about 20°C, the raw hydrogen gas is further cooled through a water cooled heat exchanger/condenser (104) where the gas temperature is cooled to about 10°C. The cooled gas containing approximately about 25% hydrogen is directed through piping (94) to the hydrogen purification system. The condensate from the heat exchanger/condenser (104) is discharged through the drain system (112).

[0079] Converting raw gas to hydrogen is economically viable as the feedstock is free or very inexpensive as compared the conventional feedstock, methane. Hydrogen however is expensive to transport as its density is very low. Using the produced hydrogen locally is then economically advantageous. Finding local uses for hydrogen is another challenge as few industrial processes use hydrogen in small quantities and they are not generally located near sources of waste gas such as landfill gas and digester biogas.

[0080] Electricity production, using PEM fuel cells for example however can be implemented anywhere and require volume flows of hydrogen that are compatible with the hydrogen production capacities of the invention. PEM fuel cells however require very pure hydrogen usually quantified as 99.999%.

[0081] In another embodiment, a hydrogen purification system (106) in accordance with the invention is shown in Fig.2 and detailed in Fig. 3.

[0082] Turning to Fig. 3, a Vacuum Pressure Swing Adsorption (VPSA) system (106) comprising a multi-adsorbent bed composed of silica gel coated activated alumina, activated carbon, lithium and 5A molecular sieve is shown in details. The VPSA (106) is composed of four vessels (148), (150), (152), (154), each vessel has, connected to the top dome of the vessel, one gas feed valve, respectively (168), (184), (198), (214), one hydrogen recovery mode valve, respectively (170), (186), (200), (216) and one pressure equalization valve, respectively (172), (188), (202), (218). Each vessel also has, connected to the bottom dome of the vessel, a pure hydrogen discharge valve, respectively (180), (194), (210), (224), an hydrogen recovery valve, respectively (174), (190), (204), (220), a blow-down & vacuum valve, respectively (182), (196), (212), (226), and a re-pressurizing valve, respectively (178), (192), (206), (222).

[0083] The hydrogen purification system (106) is composed of four vertical cylindrical vessels with raw gas top entry and bottom pure gas discharge. The purification system (106) operation cycle is in four steps as follows: step one adsorption, during which gas feed valve (168) is open and feed gas containing for example a mixture of hydrogen and carbon dioxide from which hydrogen will be separated, flows at a pressure of 2 atmospheres from the top of vessel number (148), through the adsorption bed which retains the carbon dioxide and other gaseous impurities, letting only pure hydrogen flow through.

[0084] Inside the vessel, the space above the adsorption bed is filled with the feed gas, the gas in the adsorption bed has a hydrogen concentration gradient from top to bottom going from feed gas hydrogen concentration to pure hydrogen at the bottom of the adsorption bed. The gas in the space below the adsorption bed is pure hydrogen. The produced hydrogen is directed through hydrogen discharge valve (180) which is opened at this time to the hydrogen buffer accumulator (164) then to the hydrogen compressor for storage.

[0085] While vessel number (148) is in the adsorption mode, the next vessel (150) is in the hydrogen recovery mode. During that mode, the content of vessel (152) which is in initial blow down mode, is passed through vessel (150) which is in hydrogen recovery mode. During that stage the content of the vessel in blow down mode which is composed of carbon dioxide and other gaseous impurities but contain practically no hydrogen, displaces the gas in the vessel in the hydrogen recovery mode. At the end of the hydrogen recovery mode, the gas in the vessel having completed the hydrogen recovery mode, is substantially carbon dioxide and gaseous impurities and the gas pressure in the vessel is approximately 1.95 atmospheres.

[0086] During hydrogen recovery mode of vessel (150), top valves (184) and (188) are closed and valve (186) is opened. All bottom valves of vessel (150) are closed except for valve (190) which directs the gas vented from vessel (150) to the feed gas header mixer box (166).

[0087] The gas in vessel (152) which is in the blow down mode at that time is carbon dioxide and the extraction of the gas from that vessel in the blow-down mode proceeds by suction from the vacuum pump. The vacuum pump (156) removes the free carbon dioxide gas from vessel (152) and moves it to vessel (150) which is in the hydrogen recovery mode. Once vessel (150) is full of carbon dioxide, valve (158) which connects the vacuum pump to the piping connected to the flameless combustion opens and valve (160) which connect the vacuum pump discharge to the blow-down header is close. Now the vacuum pump brings the pressure in the vessel (152) under blow-down mode to -0.05 atmosphere and vents that carbon dioxide to the flameless combustion.

[0088] The final stage in the hydrogen purification process is the re-pressurization of the vessel after blow-down and extraction of the carbon dioxide from the vessel. During the pressurization mode of vessel (154), all valves on the top side of the vessel (214), (216),

(218) are closed, all valves at the bottom side of the vessel (220), (222), (224), (226) are closed and the vessel is under vacuum, then valve (222) is opened to allow pure hydrogen from the pure hydrogen accumulator (164) to slowly re-pressurize the vessel (154) with pure hydrogen by passing through the pressurizing piping and pressure flow control valve (162). The vessel (154) may also be re-pressurized with the mixture of hydrogen and carbon dioxide from which hydrogen will be separated.

[0089] Once the pressure inside the vessel under pressurization mode reaches the nominal pressure of 1.9 atmospheres then valve (222) is closed and the vessel is ready to be pressure equalized then placed into adsorption mode by the opening of its valve (218). To perform the pressure equalizing of vessel (154), valve (172) of vessel (148) and valve (218) of vessel (154) are opened for 5 seconds then close again. After completion of the cycle time, the complete sequence starts again with vessel (154) passing to adsorption mode, vessel (148) passing to hydrogen recovery mode, vessel (150) passing to blow down mode and vessel (152) passing to pressurization mode. The cycle time can be adjusted to provide the desired hydrogen purity.

[0090] While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure that come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as follows in the scope of the appended claims.

We claim

1- A nanoparticles ceria based catalyst comprising CeO_2, at least one metal or metal oxide and at least one noble metal.

2- The nanoparticles ceria based catalyst according to claim 1, wherein the metal or metal oxide is selected from the group consiting of Fe, Ti and Sn.

3- The nanoparticles ceria based catalyst according to claim 1, wherein the noble metal is Pd and/or Pt.

4- The nanoparticles ceria based catalyst according to claim 1 wherein the catalyst has the formula $Ce_{1-x}M_xPt/Pd_yO_{2-x}$ wherein M is Fe, Ti or Sn; x varies from 0.10 to 0.33, y varies from 0.01 to 0.03.

5- A tube for a reformer comprising:

an outer surface coated with a catalyst as defined in claim 1;

a porous pipe at a first end thereof within the tube, the pipe defining an outer surface, a length and an inner passage capped at a second end opposite the first end, and

an annular passage between the pipe and the tube.

6- The tube according to claim 5, wherein the annular passage is filled with the catalyst along the length of the tube.

7- The tube according to claim 5, wherein the porous pipe outer surface is coated with the catalyst.

8- The tube according to claim 5, wherein the tube has an outside diameter of about 25 mm to about 100 mm.

9- The tube according to claim 5, wherein the pipe has an outside diameter of about 10 mm to about 70 mm.

10- A reformer comprising:

a plurality of tubes, each of which comprises an outer surface coated with a catalyst as defined in claim 1; each of the tubes having a porous pipe at a first end thereof within the tube, the pipe defining an outer surface, a length and an inner passage capped at a second end opposite the first end; and an annular passage between the pipe and the tube;

at least one inlet in communication with the reformer to introduce a raw gas to be reformed; and

at least one reformed gas outlet in communication with the reformer to discharge a reformed gas to be produced.

11- The reformer according to claim 10, wherein the annular passage is filled with a catalyst as defined in claim 1 along the length of the tube.

12- The reformer according to claim 10, wherein the porous pipe outer surface is coated with a catalyst as defined in claim 1.

13- The reformer according to claim 10, wherein the tube has an outside diameter of about 25 mm to about 100 mm.

14- The reformer according to claim 10, wherein the pipe has an outside diameter of about 10 mm to about 70 mm.

15- A system for the production of hydrogen from a raw gas comprising:

a raw gas source;

a reformer including an inlet in communication with the raw gas source for receiving the raw gas; a plurality of tubes, each of which comprises an outer surface coated with a catalyst as defined in claim 1 to promote a chemical reaction with the raw gas for producing a reformed gas; and an outlet for discharging the reformed gas produced;

a water-gas shift reactor including an inlet in communication with the outlet of the reformer for receiving the reformed gas; the catalyst for reacting the reformed gas into a mixture of hydrogen and carbon dioxide in one single shift temperature reaction step; and an outlet for discharging the mixture hydrogen and carbon dioxide; and

a separation system for the separation of the hydrogen from the carbon dioxide including an inlet in communication with the water shift reactor outlet for receiving the mixture of hydrogen and carbon dioxide; an outlet for discharging the hydrogen; and an outlet for discharging the carbon dioxide.

16- The system according to claim 15, wherein each of the tubes further comprises a porous pipe at a first end thereof within the tube, the pipe defining an inner passage capped at a second end opposite the first end, an annular passage between the pipe and the tube that is filled with the catalyst.

17- The system according to claim 15, wherein each of the tubes further comprises a porous pipe at a first end thereof within the tube; the pipe defining an outer surface and an inner passage capped at a second end opposite the first end; and an annular passage between the pipe and the tube, wherein the porous pipe outer surface is coated with the catalyst.

18- The system according to claim 15, further comprising a raw gas cleaning system in communication with the raw gas source for cleaning the raw gas prior to the injection of said raw gas into the reformer.

19- A water-gas shift reactor comprising:

a vessel having at least one inlet and at least one outlet;

a packed bed within the vessel;

a catalyst as defined in claim 1 located within the packed bed suitable for reacting in a single shift temperature reaction step a reformed gas into a mixture of hydrogen and carbon dioxide;

the at least one inlet is in communication with the vessel for receiving the reformed gas; and

the at least one outlet in communication with the vessel for discharging the mixture of hydrogen and carbon dioxide.

20- A process for the production of hydrogen from a raw gas comprising the steps of:

a) providing a raw gas;

b) introducing the raw gas into a reformer having a plurality of tubes, each of which comprises an outer surface coated with a catalyst as defined in claim 1 and a flameless combustion within each of the tubes for heating the coated outer surface of each tubes;

c) reforming the raw gas within the reformer by contacting the raw gas with the heated coated outer surface to promote a chemical reaction with the raw gas producing a reformed gas;

d) reacting the reformed gas produced in c) in the presence of the catalyst as defined above in a single shift temperature step producing a mixture of hydrogen gas and carbon dioxide; and

e) separating hydrogen from carbon dioxide produced in d).

21- The process of claim 20, wherein the flameless combustion derives from of a mixture of fuel gas and combustion air in presence of the catalyst.

22- The process according to claim 20, further comprising a step of cleaning the raw gas to be treated prior to step b).

23- The process according to claim 20, wherein the chemical reaction is carried out at a temperature of about 600°C to about 750°C.

24- The process according to claim 20, wherein the single shift temperature step is about 250°C to about 320°C.

25- The process according to claim 20, wherein the flameless combustion is heating coated outer surface of each tubes between about 550°C and about 750°C.

26- The process according to claim 20, wherein the separation of hydrogen from carbon dioxide produced in d) comprises the steps of :

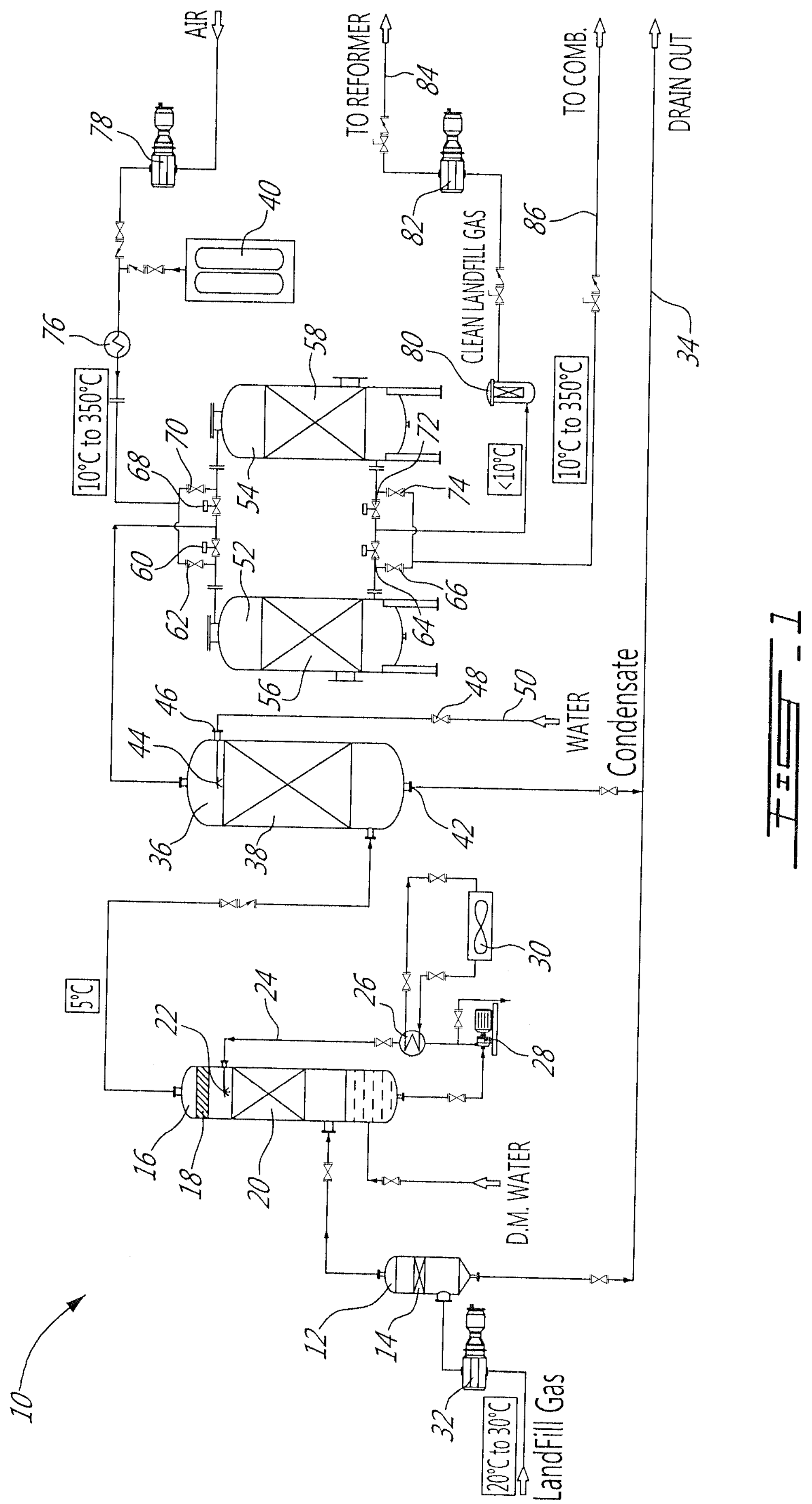
a) providing a mixture of hydrogen and carbon dioxide from which hydrogen will be separated;

b) introducing the mixture of hydrogen and carbon dioxide in a vessel comprising an adsorption bed for adsorbing the carbon dioxide and allowing passage of hydrogen therethrough to a hydrogen accumulator;

c) flushing the carbon dioxide containing an amount of hydrogen adsorbed on the adsorption bed within the vessel with carbon dioxide and transferring the carbon dioxide containing an amount of hydrogen with the mixture in a);

d) removing the carbon dioxide within the vessel and transferring to the flameless combustion; and

e) repressurizing the vessel and repeating steps b) to d).


AIR
TO REFORMER
TO COMB.
DRAIN OUT
CLEAN LANDFILL GAS
10°C to 350°C
10°C to 350°C
<10°C
5°C
WATER
Condensate
D.M. WATER
20°C to 30°C
LandFill Gas
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
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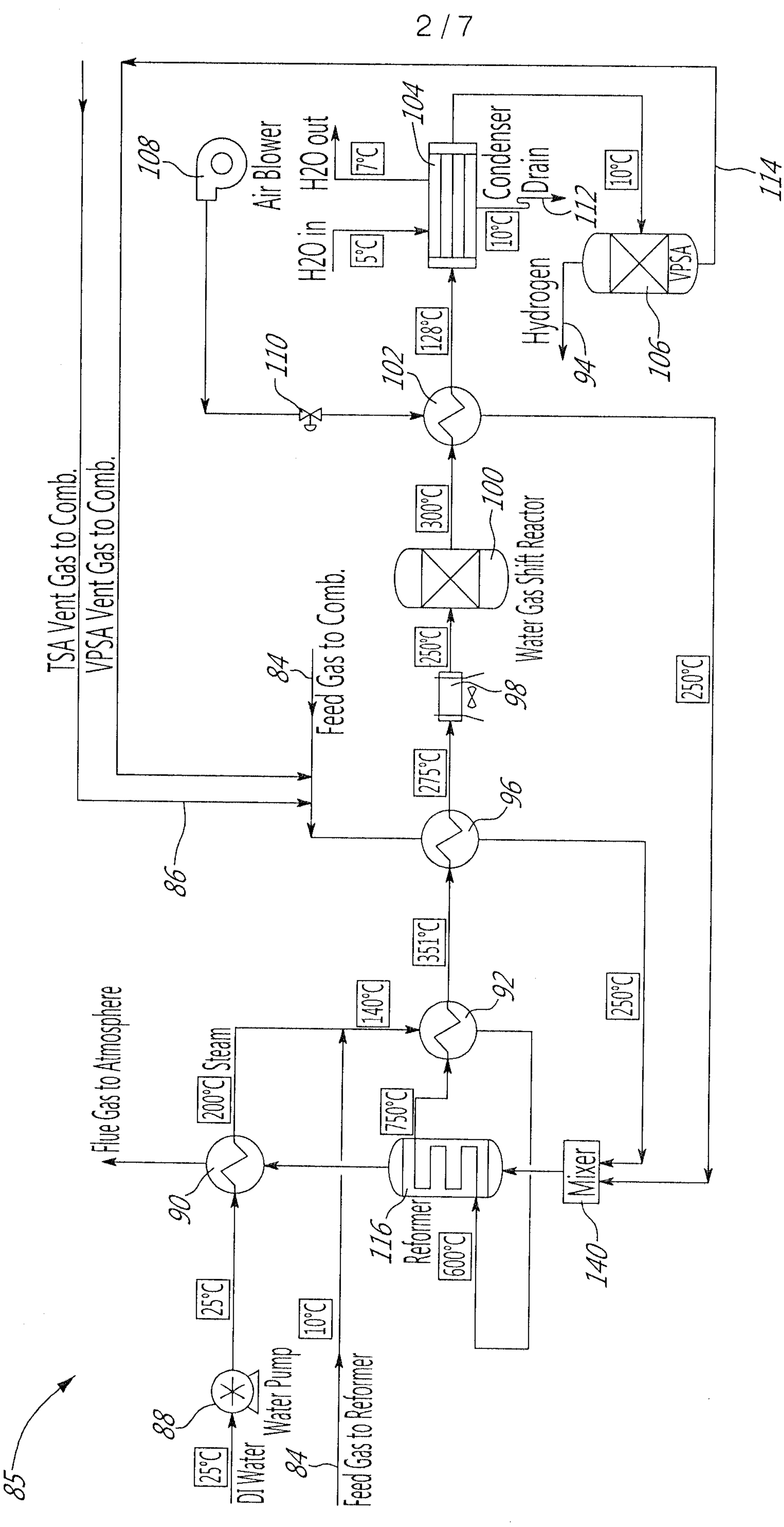
74
76
78
80
82
84
86

FIG-1



85
DI Water
25°C
88
Water Pump
25°C
90
Flue Gas to Atmosphere
200°C
Steam
84
Feed Gas to Reformer
10°C
116
Reformer
600°C
750°C
140°C
92
351°C
140
Mixer
250°C
96
275°C
98
250°C
Water Gas Shift Reactor
100
300°C
102
128°C
110
108
Air Blower
H2O in
5°C
H2O out
7°C
104
Condenser
10°C
Drain
112
10°C
VPSA
106
Hydrogen
94
114
250°C
86
TSA Vent Gas to Comb.
VPSA Vent Gas to Comb.
84
Feed Gas to Comb.

FIG. 2

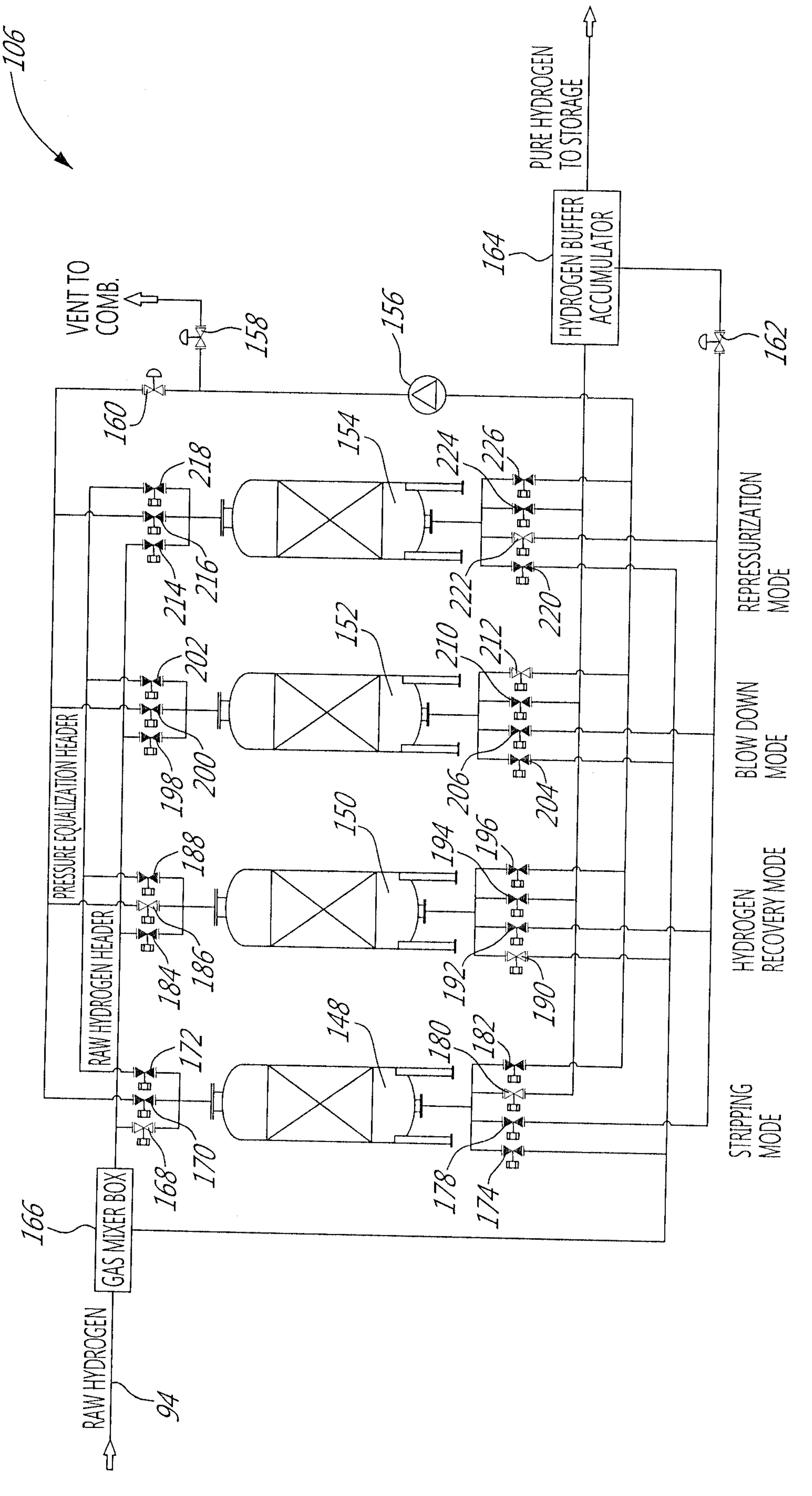

106
RAW HYDROGEN
94
GAS MIXER BOX
166
RAW HYDROGEN HEADER
PRESSURE EQUALIZATION HEADER
VENT TO COMB.
158
160
156
HYDROGEN BUFFER ACCUMULATOR
164
PURE HYDROGEN TO STORAGE
162
148
150
152
154
168
170
172
174
178
180
182
184
186
188
190
192
194
196
198
200
202
204
206
210
212
214
216
218
220
222
224
226
STRIPPING MODE
HYDROGEN RECOVERY MODE
BLOW DOWN MODE
REPRESSURIZATION MODE

FIG. 3

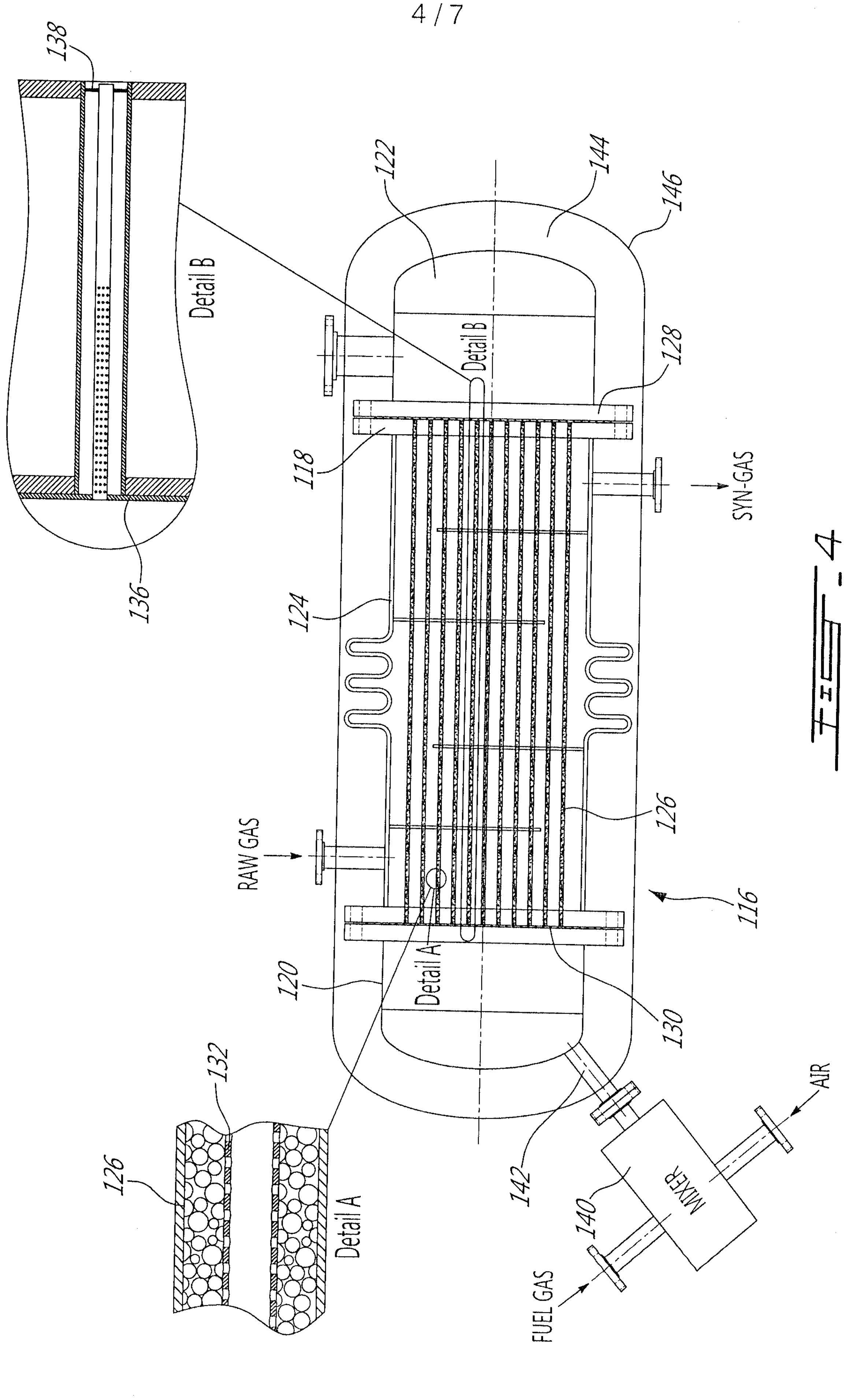

138
Detail B
136
122
144
146
Detail B
128
118
SYN-GAS
124
126
RAW GAS
116
Detail A
120
130
132
126
Detail A
142
140
MIXER
AIR
FUEL GAS

FIG. 4

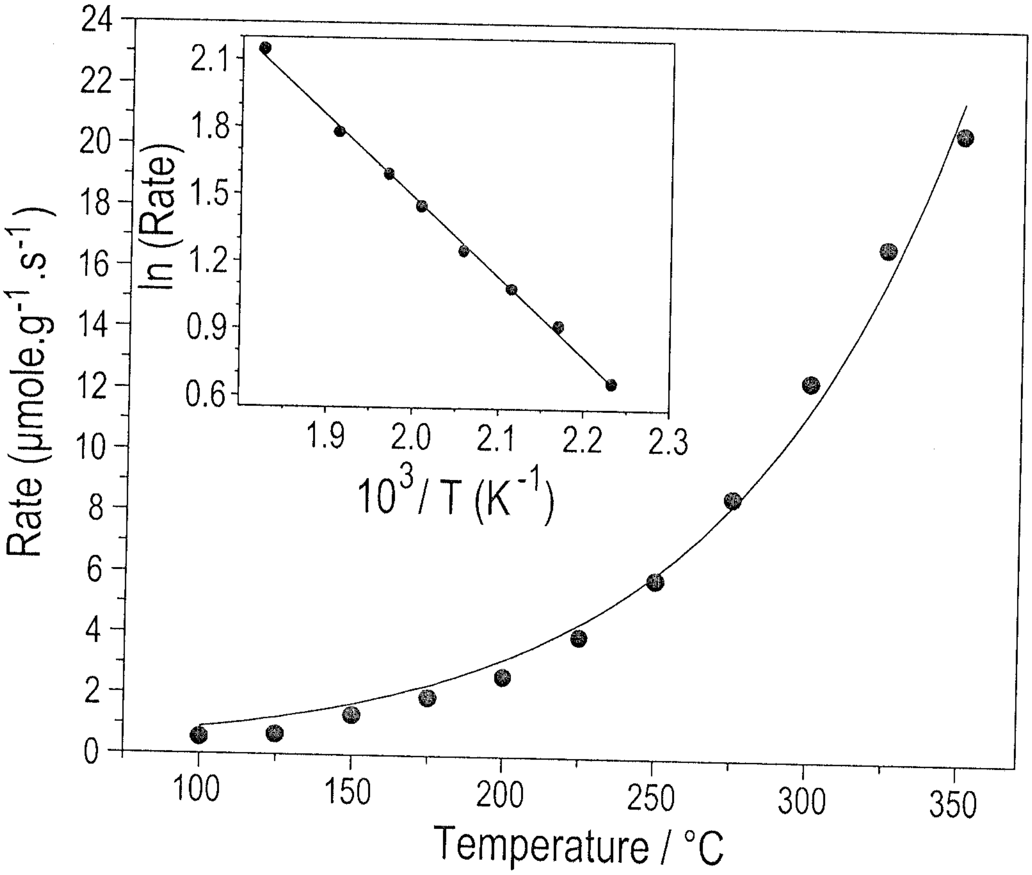

Rate (µmole.g-1.s-1)
Temperature / °C
0
2
4
6
8
10
12
14
16
18
20
22
24
100
150
200
250
300
350
ln (Rate)
10^3 / T (K^-1)
0.6
0.9
1.2
1.5
1.8
2.1
1.9
2.0
2.1
2.2
2.3

FIG. 5

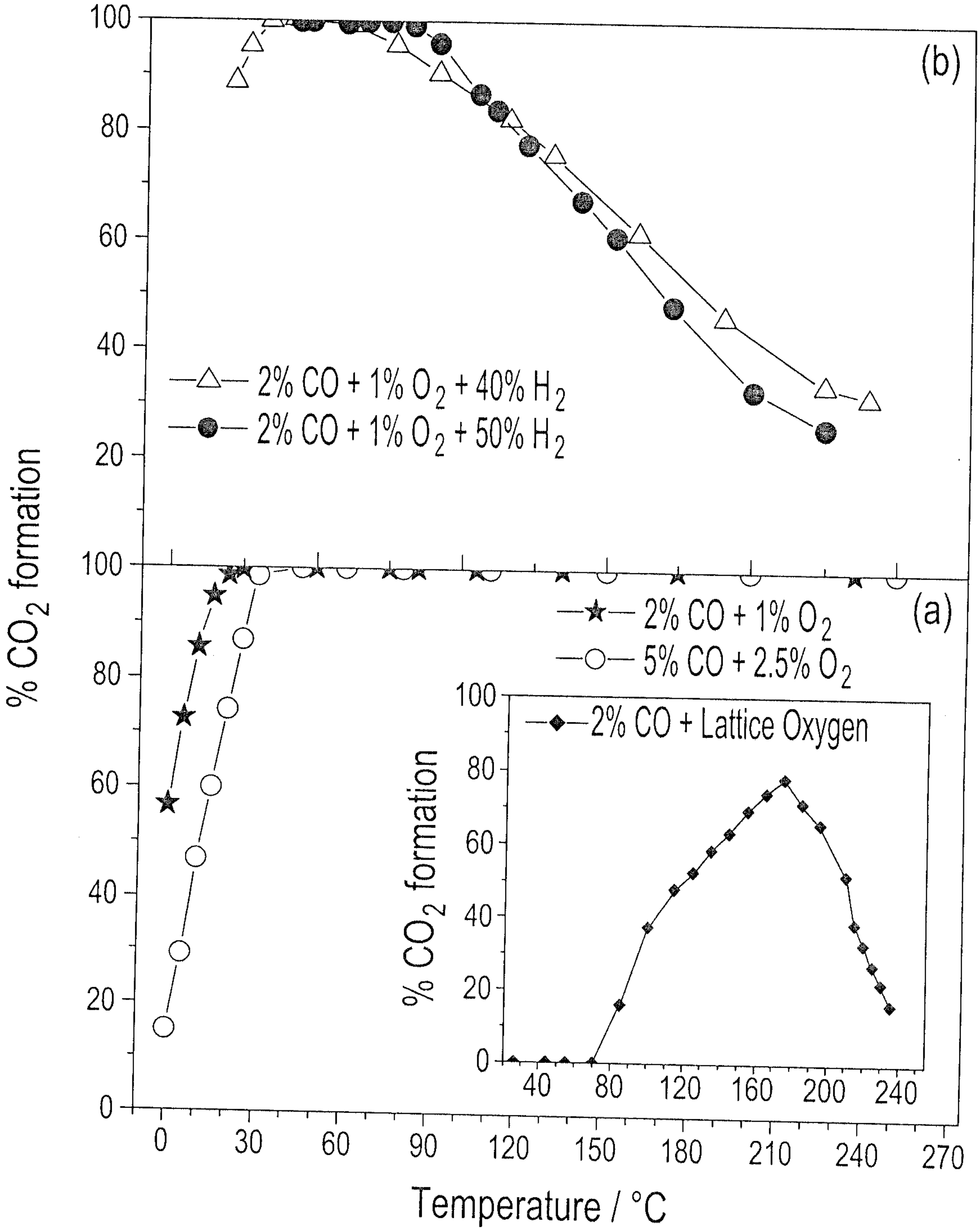

(b)
2% CO + 1% O2 + 40% H2
2% CO + 1% O2 + 50% H2
(a)
2% CO + 1% O2
5% CO + 2.5% O2
2% CO + Lattice Oxygen
% CO2 formation
Temperature / °C

FIG. 6

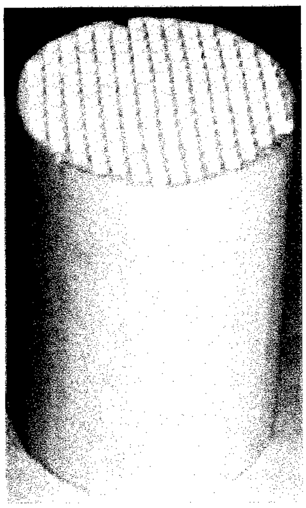


FIG. 7a

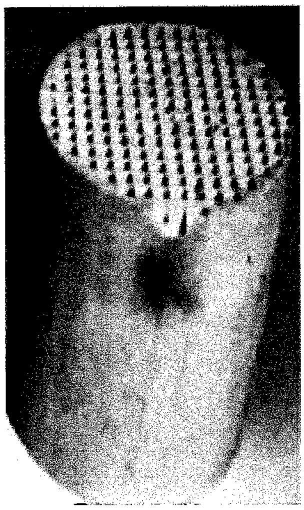


FIG. 7b

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***B01J 23/10*** (2006.01) , ***B01J 8/02*** (2006.01) , ***C01B 3/02*** (2006.01) , ***C01B 3/16*** (2006.01) , ***C01B 3/38*** (2006.01) , ***C01B 3/50*** (2006.01)
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)
IPC: B01J 23/10 (2006.01) , B01J 8/02 (2006.01) , C01B 3/02 (2006.01) , C01B 3/16 (2006.01) , C01B 3/38 (2006.01) , C01B 3/50 (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
EPOQUE, Nexis Lexis Total Patent, Canadian Patent Database (keywords: ceria, cerium (oxide), platinum, palladium, tin, iron, titanium, nanoparticle, reformer, tube, outer, coat(ing), gas, shift)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US2009298683 A1 (LOMELLO-TAFIN, M. et al.) 03 December 2009 (03-12-2009) * abstract, examples, claims *	1-4
X Y	WO2006034103 A1 (WELLINGTON, S. et al.) 30 March 2006 (30-03-2006) * page 5, line 22-page 6, line 3; page 21, line 9-page 26, line 7; figures *	5-14, 20, 23-25 22
X Y	CA2396402 A1 (KLUG, K.) 29 January 2004 (29-01-2004) * figures; [0015] - [0019]; [0048] *	5-14 15-18
X Y	US2005097819 A1 (LOMAX, F. et al.) 12 May 2005 (12-05-2005) * figures, [0081], claims *	19 15-18, 22
X Y	WO2004022480 A2 (MATZAKOS, A. et al.) 18 March 2004 (18-03-2004) * whole document *	20, 23-25 21-22
Y	CA2685299 A1 (LYGOURAS, D. et al.) 04 December 2008 (04-12-2008) * figures; page 8, line 4-22; page 10, line 6-21; page 13, line 1-32 *	20-21

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

* Special categories of cited documents :
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier 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
10 March 2011 (10-03-2011)	20 April 2011 (20-04-2011)

Name and mailing address of the ISA/CA	Authorized officer
Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Wendy PYSYK (819) 994-1591

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons :

1. [ ] Claim Nos. :
   because they relate to subject matter not required to be searched by this Authority, namely :

2. [ ] Claim Nos. :
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :

3. [ ] Claim Nos. :
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows :

See Supplemental Box III.

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [X] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. :

Remark on Protest [ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US2007183968 A1 (HEALEY, T. et al.) 09 August 2007 (09-08-2007) * whole document *	1-26
A	WO2009028113 A1 (NAGAOKA, K. et al.) 05 March 2009 (05-03-2009) & EP2184104A1 12 MAY 2010 (12-05-2010) * whole document *	1-26

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Continuation of Supplemental Box III.

Reference is made to the following documents:

D1 - US2009298683 A1 (LOMELLO-TAFIN, M. et al.) 03 December 2009 (03-12-2009)
D2 - WO2006034103 A1 (WELLINGTON, S. et al.) 30 March 2006 (30-03-2006)
D3 - CA2396402 A1 (KLUG, K.) 29 January 2004 (29-01-2004)
D4 - US2005097819 A1 (LOMAX, F. et al.) 12 May 2005 (12-05-2005)
D5 - WO2004022480 A2 (MATZAKOS, A. et al.) 18 March 2004 (18-03-2004)
D6 - CA2685299 A1 (LYGOURAS, D. et al.) 04 December 2008 (04-12-2008)
D7 - US2007183968 A1 (HEALEY, T. et al.) 09 August 2007 (09-08-2007)
D8 - WO2009028113 A1 (NAGAOKA, K. et al.) 05 March 2009 (05-03-2009)

The claims are directed to a plurality of inventive concepts as follows:

Group A - Claims 1-4 are directed to a nanoparticle ceria based catalyst comprising CeO2, at least one metal or metal oxide and at least one noble metal.
Group B - Claims 5-14 and 17 are directed to a system comprising a reformer, water-gas shift reactor and a separator, the reformer comprising a plurality of tubes and the tubes comprising a porous pipe and a catalyst coating on the outer surface.
Group C - Claims 15, 16, 18 is directed to a system for the production of hydrogen from a raw gas comprising a reformer (different from Group B), water-gas shift reactor and a separation system.
Group D - Claim 19 is directed to a water-gas shift reactor.
Group E - Claim 20-26 is directed to a process for the production of hydrogen from a raw gas comprising a reforming a raw gas in a reformer having flameless combustion within each tube, a single shift temperature step and a separation step.

The claims must be limited to one inventive concept as set out in Rule 13 of the PCT.

An a posteriori analysis has concluded that the catalyst of claim 1 is not considered new with regard to D1 and since all claims are dependent on the catalyst of claim 1 there is no unifying concept in the claims. D7and D8 teach the state of the art and that the catalyst components are known for use in reforming and water gas shift reactions.

Groups B-E were searched with no basis to the catalyst of claim 1.