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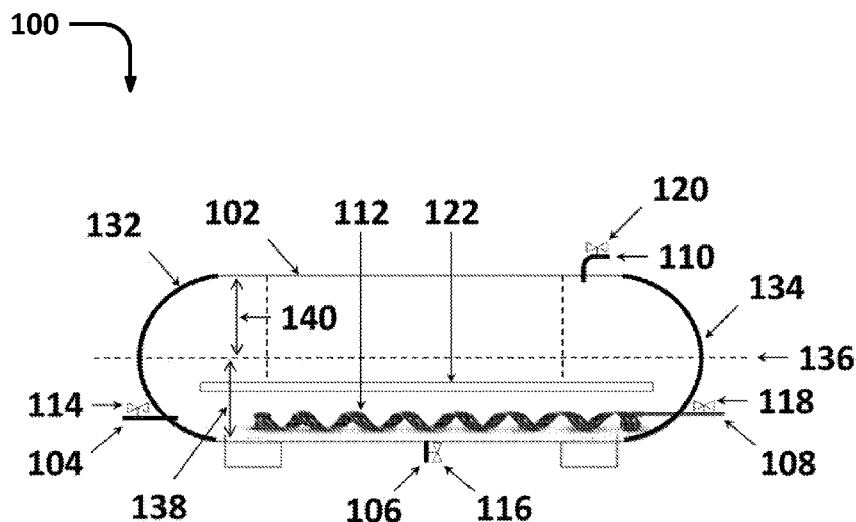


Fig. 1A

(57) **Abstract:** A water splitting system, whereby hydrogen is produced from water dissociation in presence of a photocatalyst and solar radiation in a photocatalytic water splitting reactor, wherein a natural gas stream is continuously agitating a catalyst slurry comprising water and the photocatalyst, to improve hydrogen production yield and to dilute gaseous products below explosive limits. Various embodiments of the photocatalytic water splitting reactor, and the water splitting system are also provided.



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TITLE

USING NATURAL GAS AS AGITATING GAS FOR PHOTOCATALYTIC
WATER SPLITTING

5

BACKGROUND OF THE INVENTION

TECHNICAL FIELD

The present invention relates to a photocatalytic water splitting reactor, a water splitting system, and a method of using the same to split water using natural gas.

10 DESCRIPTION OF THE RELATED ART

The “background” description provided herein is for the purpose of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description which may not otherwise qualify as prior art at the time of filing, are neither expressly or impliedly admitted
15 as prior art against the present invention.

Hydrogen is the simplest and most abundant element in the universe. Almost 75% of the universe mass consists of hydrogen, a colorless, odorless, non-toxic, and nonmetallic gas. Although hydrogen does not occur naturally, it can always be found combined with other elements such as water and organic compounds. A number of recent studies suggest that the
20 direct use of hydrogen as a fuel may provide a much cleaner and far less expensive fuel alternative. Almost no pollution is produced by engines that burn hydrogen. In addition, hydrogen is high in energy content, and is currently a useful feedstock in a diversity of industries. Most cracking and reforming processes in petrochemical industries and petroleum refineries use hydrogen as a feedstock for the reactors. Furthermore, various hydrogenation
25 processes consume hydrogen to produce higher value chemicals (e.g. ammonia productions

and/or urea/fertilizers). Moreover, it can be envisioned that hydrogen could be a future energy source for homes, businesses, industries and particularly for transportation.

Nowadays, hydrogen is being produced in large quantities for industrial and commercial purposes. However, most hydrogen production plants require fossil fuels. These plants largely use natural gas, coal, petroleum feedstocks or even nuclear energy to generate electricity to either electrolyze water, or to steam reformat natural gas to produce hydrogen. The process of water-splitting is a highly endothermic process and for this reason, hydrogen is mostly produced from natural gas. The challenge is to produce hydrogen from renewable resources and with inexpensive manufacturing cost.

Various studies have been conducted to investigate photocatalytic water splitting as a means to generate hydrogen directly from water using sunlight. Photocatalytic water splitting is not only a renewable means toward hydrogen production, but also the amount of greenhouse gases (particularly carbon-dioxide) formed as a result of hydrogen production is substantially lower than other existing methods.

US 8,709,132 relates to a water dissociating system, whereby hydrogen is produced via thermolysis (i.e. water dissociation by thermal energy), wherein the thermal energy is supplied by an absorption element which is heated by solar energy. EP 2,630,086 relates to a method of producing hydrogen from ethanol/water mixture over a photocatalyst (TiO_2). Other studies have been conducted toward generating electricity from solar energy using solar cells, and subsequently transferring the generated electricity to an electrochemical cell to electrolyze water and to produce hydrogen.

In view of the forgoing, one objective of the present invention relates to a water splitting reactor and system for splitting water that involves agitating a catalyst slurry with natural gas.

BRIEF SUMMARY OF THE INVENTION

According to a first aspect the present disclosure relates to a photocatalytic water splitting reactor, involving i) a horizontally oriented vessel with a first and a second end separated by a side wall along a longitudinal axis of the vessel and an internal cavity
5 configured to hold a liquid phase proximal to the bottom of the vessel and a gas phase proximal to the top of the vessel, ii) a liquid phase inlet and a first valve attached to the liquid phase inlet located proximal to the bottom of the vessel, iii) a liquid phase outlet and a second valve attached to the liquid phase outlet located proximal to the bottom of the vessel, iv) a gas inlet and a third valve attached to the gas inlet located proximal to the bottom of the vessel, v)
10 a perforated tube fluidly connected to the gas inlet, wherein the perforated tube has a longitudinal axis that is parallel to the longitudinal axis of the vessel and is located proximal to the bottom of the vessel, vi) a gas outlet and a fourth valve attached to the gas outlet located proximal to the top of the vessel, vii) wherein the liquid phase inlet and the liquid phase outlet are adapted for loading and unloading the vessel with the liquid phase, and
15 wherein the perforated tube is configured to disperse the gas phase into the liquid phase.

In one embodiment, the perforated tube is straight and located along the side wall of the vessel. In one embodiment, the perforated tube is helically extended along the longitudinal axis of the vessel. In one embodiment, the perforated tube has perforations that are equally spaced apart around the circumference and along a length of the perforated tube.

20 In one embodiment, the liquid phase inlet, the liquid phase outlet, and the gas inlet are located on the first end of the vessel.

In one embodiment, the reactor further comprises a light source located inside the vessel and is configured to be submerged in the liquid phase, wherein the light source generates visible light and/or UV light. In one embodiment, the light source is in the form of

an elongated structure that has a longitudinal axis which is parallel to the longitudinal axis of the vessel.

In one embodiment, the vessel is made of a transparent material to expose the internal cavity to sunlight.

5 In one embodiment, the reactor further comprises a heating/cooling jacket which covers a portion of an external surface of the vessel.

According to a second aspect the present disclosure relates to a water splitting system, involving i) the photocatalytic water splitting reactor, and ii) a natural gas source located upstream of and fluidly connected to the gas inlet of the photocatalytic water splitting reactor
10 via a natural gas line, wherein the natural gas source supplies a natural gas to the photocatalytic water splitting reactor to agitate the liquid phase, which comprises water and a photocatalyst, to dissociate water in presence of the photocatalyst to form hydrogen and oxygen.

In one embodiment, the system further comprises a first gas separation unit located
15 downstream of and fluidly connected to the gas outlet of the photocatalytic water splitting reactor via a product gas line, wherein the first gas separation unit is configured to receive the oxygen, the hydrogen, and the natural gas from the photocatalytic water splitting reactor and to remove hydrogen to form a hydrogen stream and a fuel stream comprising oxygen and the natural gas.

20 In one embodiment, the system further comprises a second gas separation unit located downstream of and fluidly connected to the first gas separation unit via a first reflux line, and is configured to remove oxygen from the fuel stream to form an oxygen stream and a methane-rich stream.

In one embodiment, the system further comprises a combustor located downstream of
25 and fluidly connected to the first gas separation unit, wherein the fuel stream is combusted.

In one embodiment, the system further comprises a second reflux line which fluidly connects the second gas separation unit to a gas mixer, which is located downstream of the second gas separation unit and upstream of the photocatalytic water splitting reactor, wherein the second reflux line delivers the methane-rich stream to the gas mixer, wherein the
5 methane-rich stream is combined with the natural gas to form a recycle stream.

In one embodiment, the system further comprises a third reflux line which fluidly connects the gas mixer to the gas inlet of the photocatalytic water splitting reactor, wherein the third reflux line delivers the recycle stream to the photocatalytic water splitting reactor.

In one embodiment, the system further comprises a light source which is located
10 inside the photocatalytic water splitting reactor and is configured to be submerged in the liquid phase.

In one embodiment, the first and the second gas separation units are pressure swing adsorption units.

In one embodiment, the natural gas comprises methane and one or more of ethane,
15 carbon dioxide, nitrogen, and hydrogen sulfide.

According to a third aspect the present disclosure relates to a method of photocatalytic water splitting, involving i) exposing a liquid phase comprising water and a photocatalyst to visible light and/or UV light within an internal cavity of a photocatalytic water splitting reactor while concurrently agitating the liquid phase with a natural gas from a natural gas
20 source to dissociate water to form hydrogen and oxygen, ii) collecting the hydrogen, the oxygen, and the natural gas, iii) separating the hydrogen in a first gas separation unit to form a hydrogen stream and a fuel stream comprising the oxygen and the natural gas.

In one embodiment, the method further comprises removing the oxygen from the fuel stream in a second gas separation unit to form an oxygen stream and a methane-rich stream.

In one embodiment, the method further comprises mixing the methane-rich stream and the natural gas in a gas mixer to form a recycle stream, and delivering the recycle stream to the photocatalytic water splitting reactor.

In one embodiment, the method further comprises delivering the hydrogen stream to a
5 hydroprocessing and/or hydrotreating unit.

In one embodiment, the method further comprises delivering the fuel stream to a power plant and/or ammonia production plant.

The foregoing paragraphs have been provided by way of general introduction, and are not intended to limit the scope of the following claims. The described embodiments, together
10 with further advantages, will be best understood by reference to the following detailed description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the disclosure and many of the attendant advantages
15 thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

Fig. 1A illustrates a horizontally oriented photocatalytic water splitting reactor.

Fig. 1B illustrates an end-on view of the horizontally oriented photocatalytic water
20 splitting reactor filled with catalyst slurry, wherein all liquid/gas inlets and outlets are located on one end of the reactor.

Fig. 2 illustrates a vertically oriented photocatalytic water splitting reactor filled with catalyst slurry.

Fig. 3A illustrates an embodiment of the water splitting system.

25 Fig. 3B illustrates an alternative embodiment of the water splitting system.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Referring now to the drawings, wherein like reference numerals designate identical or corresponding parts throughout the several views.

5 According to a first aspect the present disclosure relates to a photocatalytic water splitting reactor 100, involving a horizontally oriented vessel 102 with a first 132 and a second end 134 separated by a side wall along a longitudinal axis 136 of the vessel and an internal cavity configured to hold a liquid phase proximal to the bottom of the vessel 138 and a gas phase proximal to the top of the vessel 140 (see Fig. 1A).

10 In terms of the present disclosure, a photocatalytic water splitting reactor refers to a vessel or a container, wherein a water splitting reaction is conducted. “Photocatalytic water splitting reactor” and “reactor” are identical in the context of the present disclosure, and thus may be used interchangeably.

 The water splitting reaction refers to a chemical reaction whereby water is
15 decomposed into its constituent elements (i.e. oxygen and hydrogen). The water splitting reaction can be performed in several ways. For example, electrolysis (i.e. decomposition of water into oxygen and hydrogen gas by passing an electric current through water), photoelectrolysis (i.e. decomposition of water by passing a photo-generated electric current), thermolysis (i.e. decomposition of water at extremely high temperature), radiolysis (i.e.
20 decomposition of water via nuclear radiation), photobiological water splitting, and so forth, however, the water splitting reaction as used herein refers to photocatalytic water splitting or photocatalysis, wherein water is directly decomposed to its constituent elements by solar radiation (or sunlight), and/or other type of natural or artificial light sources in the presence of a photocatalyst.

Photocatalysis can be homogenous or heterogeneous. Homogenous photocatalysis may refer to a case where reactants and the photocatalyst are present in the same phase and form a homogeneous mixture, whereas heterogeneous photocatalysis may refer to a case where reactants and the photocatalyst are in different phases (for example a solid phase catalyst and a gaseous phase reaction mixture). In one embodiment, the photocatalysis in this disclosure involves heterogeneous photocatalysis.

The vessel 102 refers to a container that is designed to hold gas and liquids preferably at temperatures and pressures above ambient temperature and pressure. The vessel 102 may be made of stainless steel, nickel steel, chromium steel, aluminum, aluminum alloy, copper and copper alloys, titanium, and the like, although the materials used to construct the vessel are not meant to be limiting and various other materials may also be used. In a preferred embodiment, the vessel is made of a transparent material to expose the internal cavity to sunlight. Exemplary transparent materials include, but are not limited to glass, general purpose polystyrene (GPPS), polycarbonate (PC), poly methyl methacrylate (PMMA), styrene acrylonitrile (SAN), styrene methyl methacrylate (SMMA), polyethylene terephthalate glycol-modified (PET-G), methyl metacrylate butadiene styrene (MBS), and/or any combination thereof. Additionally, a transparent vessel may also have one or more mirrors located inside the vessel and attached to the side wall at the bottom of the vessel, with no gap therebetween, wherein the mirrors reflect the sunlight to enhance the photocatalysis. In another embodiment, the mirrors are located outside and below the bottom of the vessel, wherein the mirrors reflect the sunlight to enhance the photocatalysis.

In a preferred embodiment, the vessel 102 is cylindrical having an internal volume in the range of $0.5 - 1000 \text{ m}^3$, or preferably $10 - 100 \text{ m}^3$, or preferably $10 - 50 \text{ m}^3$, or preferably $10 - 40 \text{ m}^3$, or preferably $10 - 30 \text{ m}^3$, or preferably $10 - 20 \text{ m}^3$. The vessel has a preferable length (L) in the range of $0.5 - 20 \text{ m}$, or preferably $1 - 10 \text{ m}$, or preferably $2 - 10 \text{ m}$, or

preferably 3 – 10 m, or preferably 4 – 10 m, or preferably 5 – 10 m, and an internal diameter (D) in the range of 0.01 – 3 m, preferably 0.2 – 2 m, or preferably 0.2 – 1.5 m, or preferably 0.2 – 1 m, or preferably 0.5 – 1 m. A relative ratio of the length to the inner diameter (L/D) of the vessel may be in the range of 5 – 500, preferably 50 – 500, more preferably 50 – 100, or 5 preferably around 50. The vessel may have a wall thickness in the range of 1 – 20 cm, or preferably 2 – 10 cm, or preferably 5 – 10 cm.

In one embodiment, the horizontally oriented vessel is a cylindrical vessel with a longitudinal axis parallel to ground surface. The side wall refers to a lateral wall that is extended along and parallel to the longitudinal axis of the vessel, which is bound by the first and the second end, wherein the first and the second end are substantially similar and may be secured perpendicular to the side wall. In one embodiment, the first and the second end are flat and circular having a diameter that is substantially similar to the internal diameter of the vessel. In another embodiment, the first and the second end are hemispheres having a diameter that is substantially similar to the internal diameter of the vessel. In one embodiment, the vessel 102 has a spherical geometry. The vessel may also have other geometries including, but not limited to conical, rectangular, and pyramidal.

Other than inlets/outlets designed to allow ingress and egress, the vessel may be perfectly sealed to prevent any leakage of the liquid phase and/or the gas phase.

“Proximal to the bottom” refers to a region in the internal cavity that is located less than 50%, preferably less than 40%, more preferably less than 30% of the diameter of the vessel when measured from the bottom of the vessel, with 0% being the bottom and 100% being the top of the cylindrical vessel. Accordingly, “proximal to the top” refers to a region in the internal cavity that is located at least 50%, preferably at least 60%, more preferably at least 70% from the bottom of the vessel with 0% being the bottom and 100% being the top of the cylindrical vessel. For example, if the horizontal cylinder is filled to 30% total volume

capacity with a liquid phase, then the liquid level is located at 30% from the bottom of the vessel and thus the liquid may be considered “proximal to the bottom”.

In one embodiment, the reactor 100 further comprises a heating/cooling jacket which covers a portion of an external surface of the vessel 102. The heating/cooling jacket may be a
5 heat exchanger that is secured on and in direct contact with the external surface of the vessel. The heating/cooling jacket may be used to maintain the temperature of the liquid phase inside the vessel in the range of 10 – 80 °C, or preferably 20 – 60 °C, or preferably 40 – 60 °C. In one embodiment, the heating/cooling jacket is an elongated conduit which is helically extended around the circumference and along the length of the vessel, wherein a
10 heating/cooling medium, which can be an aqueous glycol solution, water, a fluorocarbon, and the like, is circulated in the elongated conduit. The temperature inside the vessel may be controlled by a computer-controlled unit. In one embodiment, the heating/cooling jacket covers 10 – 100%, preferably 50 – 90%, more preferably 50 – 80% and most preferably about 70% of the external surface area of the vessel. Alternatively, in another embodiment, the
15 heating/cooling jacket covers 10 – 100%, preferably 50 – 90%, or preferably 50 – 80%, or preferably 50 – 70%, or preferably about 70% of the length of the vessel.

The photocatalytic water splitting reactor 100 includes a liquid phase inlet 104 and a first valve 114 attached to the liquid phase inlet located proximal to the bottom of the vessel 102. Further, the photocatalytic water splitting reactor 100 includes a liquid phase outlet 106
20 and a second valve 116 attached to the liquid phase outlet located proximal to the bottom of the vessel.

The liquid phase inlet 104 and the liquid phase outlet 106 may be adapted for loading and unloading the vessel 102 with the liquid phase. In one embodiment, the liquid phase inlet and the liquid phase outlet are substantially similar, wherein each is a cylindrical port having
25 an internal diameter in the range of 1 – 20 cm, preferably 2 – 10 cm, or preferably 2 – 5 cm,

and configured to transfer a liquid flow in the flow rate of 10 – 1000 l/min, preferably 10 – 200 l/min, or preferably 50 – 100 l/min. In another embodiment, the liquid phase inlet and the liquid phase outlet are located on the same end (for example the first end) and proximal to the bottom of the vessel. In one embodiment, the liquid phase inlet is located on the first end and
5 the liquid phase outlet is located on the second end, while both are proximal to the bottom of the vessel. In a preferred embodiment, the liquid phase inlet is located on the first end and proximal to the bottom of the vessel, and the liquid phase outlet is located on the side wall at the bottom of the vessel.

In one embodiment, the first and the second valves may be a gate valve or a globe
10 valve and may also be used to control a flow rate of the liquid phase.

The photocatalytic water splitting reactor 100 involves a gas inlet 108 and a third valve 118 attached to the gas inlet located proximal to the bottom of the vessel 102. Further, the photocatalytic water splitting reactor 100 involves a gas outlet 110 and a fourth valve 120 attached to the gas outlet located proximal to the top of the vessel. The gas inlet and the gas
15 outlet may be utilized for loading and unloading the vessel with the gas phase. In one embodiment, the gas inlet and the gas outlet are substantially similar, wherein each is a cylindrical port having an internal diameter in the range of 1 – 10 cm, preferably 1 – 5 cm, or preferably 1 – 2 cm, and configured to transfer a gas flow in the flow rate of 10 – 1000 l/min, preferably 10 – 200 l/min, or preferably 50 – 100 l/min. In a preferred embodiment, the gas
20 inlet is located on the side wall and proximal to the bottom of the vessel, and the gas outlet is located on the side wall and proximal to the top of the vessel. In another preferred embodiment, the gas inlet is located on one end and proximal to the bottom of the vessel, and the gas outlet is located on the side wall and proximal to the top of the vessel.

In one embodiment, the third and the fourth valves may be a check valve or a diaphragm valve. The third and the fourth valves may also be used to control a flow rate of the gas phase.

In another embodiment, the liquid phase inlet 104, the liquid phase outlet 106, the gas inlet 108, and the gas outlet 110 are located on the first end of the vessel 102, wherein the liquid phase inlet, the liquid phase outlet, and the gas inlet are proximal to the bottom of the vessel, and the gas outlet is proximal to the top of the vessel.

In one embodiment, a safety valve is adapted for the vessel 102 and is located proximal to the top of the vessel, wherein the safety valve regulates internal pressure of the vessel by opening a pathway for the gas phase to leave the internal cavity of the vessel in circumstances when excessive pressure is accumulated in the internal cavity.

The photocatalytic water splitting reactor 100 further involves a perforated tube 112 fluidly connected to the gas inlet 108 and is configured to be submerged in the liquid phase and to disperse/bubble a gaseous flow into the liquid phase. In a preferred embodiment, the perforated tube has a longitudinal axis that is parallel to the longitudinal axis of the vessel and is located proximal to the bottom of the vessel. In another embodiment, the perforated tube is located along the side wall of the vessel. The perforated tube may be rectangular tubing (i.e. having a rectangular cross section), or preferably round tubing (i.e. having a round cross section), which is straight or preferably extended helically along the longitudinal axis of the vessel. In a preferred embodiment, the end of the perforated tube that is not connected to the gas inlet is sealed. In one embodiment, the perforated tube has perforations that are equally spaced apart around the circumference and along a length of the perforated tube. In another embodiment, the perforations are equally spaced apart along a straight line that is parallel to the longitudinal axis of the perforated tube. The direction of gas flow inside the perforated tube may preferably be parallel to the longitudinal axis of the vessel, while the direction of

gas flow outwardly from the perforated tube may be perpendicular to the longitudinal axis of the perforated tube when exiting the perforations. In one embodiment, the perforated tube has perforations with no specific pattern. The perforations are substantially similar, preferably circular, having a diameter in the range of 0.5 – 5 mm, preferably 1 – 3 mm, more preferably about 1 mm. The perforated tube may have a length of at least 5 m, preferably at least 10 m, or preferably at least 15 m, or preferably at least 20 m with respect to the length of the vessel which is in the range of 0.5 – 20 m, or preferably 1 – 10 m, or preferably 2 – 10 m, or preferably 3 – 10 m, or preferably 4 – 10 m, or preferably 5 – 10 m. The inner diameter of the perforated tube may be in the range of 1 – 10 cm, preferably 1 – 5 cm, or preferably 1 – 2 cm with respect to the internal diameter of the gas inlet, and the thickness of the perforated tube may be in the range of 3 – 50 mm, preferably 5 – 20 mm, more preferably 5 – 10 mm, although other dimensions are possible and the perforated tube may still function as intended.

In one embodiment, the reactor 100 further comprises a light source 122 located inside the vessel 102 and attached to the top of the vessel, wherein the light source generates visible light and/or UV light. In one embodiment, the light source is configured to be located in the gas phase. In a preferred embodiment, the light source is configured to be submerged in the liquid phase. In one embodiment, the light source is a light bulb or a plurality of light bulbs attached to the top of the vessel. In one embodiment, the light source is an elongated fluorescent tube or structure (e.g. a generally rectangular shape) that has a longitudinal axis parallel to the longitudinal axis of the vessel, wherein the elongated fluorescent tube or structure is attached to the side wall either from the top or the bottom of the vessel.

Referring now to Fig. 2. In one embodiment, the reactor 100 is a vertically oriented cylindrical vessel (or vertically oriented reactor) with the first and the second end separated by a vertical side wall along the longitudinal axis of the vessel and the internal cavity configured to hold the liquid phase proximal to the bottom of the vessel and the gas phase

proximal to the top of the vessel. The liquid phase inlet 104 and liquid phase outlet 106 may be located on the vertical side wall and proximal to the bottom of the vertically oriented reactor, whereas the gas inlet 108 and the gas outlet 110 may be located on the first end and proximal to the top of the vertically oriented reactor. In one embodiment, the vertically oriented reactor further comprises the perforated tube 112, which is helically extended along the longitudinal axis of the vertically oriented reactor and may be sealed preferably by a cap 242, the safety valve 230, and the light source 122. The light source may be a plurality of light bulbs that are located inside the vertically oriented reactor. In another embodiment, the vertically oriented reactor may involve an agitating system comprising a propeller 236, which is located inside the vertically oriented reactor, a motor 240, which is located outside and preferably at the top of the vertically oriented reactor, and a shaft 238, which connects the propeller 236 to the motor 240. In a preferred embodiment, the vertically oriented reactor further involves a heating/cooling jacket 244 which covers a portion of an external surface area of the vertically oriented reactor to maintain the temperature of the liquid phase inside the vessel in the range of 10 – 80 °C, preferably 20 – 60 °C, or preferably 20 – 40 °C. In one embodiment, the heating/cooling jacket covers 10 – 100%, preferably 50 – 90%, and more preferably 50 – 80% of the external surface area of the vertically oriented reactor.

According to a second aspect the present disclosure relates to a water splitting system 300. The water splitting system as used herein refers to a set of operational units, including the photocatalytic water splitting reactor, that are fluidly connected and are used to produce hydrogen and oxygen through the photocatalysis of water in the reactor, and further processing the hydrogen and/or oxygen, for example to form separate hydrogen rich and oxygen rich streams.

A catalyst slurry refers to a mixture of water and photocatalyst particles (and optionally other materials such as a sacrificial agent), wherein the photocatalyst particles are

solid particles that are suspended in water forming a heterogeneous mixture. The water can be distilled water, fresh water, brackish water, saline water, or brine.

The photocatalyst refers to a material (preferably a semiconductor) that is not consumed in the photocatalysis while concurrently accelerating the photocatalysis by
5 absorbing a light photon.

In a preferred embodiment, the photocatalyst 234 is granular having suspended solid particles in the catalyst slurry with an average particle size of at least 20 nm, preferably at least 15 nm, or preferably at least 10 nm, or preferably at least 5 nm. Nanosized photocatalyst particles provide greater surface area wherein photocatalysis takes place, and thus give
10 superior hydrogen generation yield. Exemplary photocatalysts include, but are not limited to metal oxide semiconductors, including TiO_2 , SrTiO_3 , $\text{Na}_2\text{Ti}_6\text{O}_{13}$, BaTi_4O_9 , Ta_2O_5 , KTaO_3 , $\text{K}_4\text{Nb}_6\text{O}_{17}$, $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, ZnO , Zn -doped ZnO , or metal sulfide semiconductors, including CdS , ZnS , VS , VS_4 , WO_3 , RuS_2 , or Ni - and Cu -doped metal sulfide semiconductors, or even coupled semiconductors, including CdS/TiO_2 , ZnS/TiO_2 , $\text{Cu}_2\text{O}/\text{TiO}_2$, CuO/TiO_2 , WO_3/SiC –
15 TiO_2 , $\text{SrTiO}_3/\text{TiO}_2$, $\text{SnO}_2/\text{TiO}_2$, RuO_2 – Pt -loaded $\text{TiO}_2\text{Ta}_2\text{O}_3/\text{TiO}_2$, and $\text{CuO}/\text{Al}_2\text{O}_3/\text{TiO}_2$.

In one embodiment, the catalyst slurry 232 further includes a sacrificial agent. Exemplary sacrificial agents include, but are not limited to glycerol, sodium sulfide, preferably organic compounds such as methanol, ethanol, propanol, formic acid, and/or oxalic acid.

20 In one embodiment, the catalyst slurry 232 is exposed to UV light, wherein the photocatalyst is a UV-based photocatalyst. In a preferred embodiment, the catalyst slurry is exposed to visible light (e.g. solar radiation/sunlight), wherein the photocatalyst is a visible light photocatalyst.

In one embodiment, the catalyst slurry is prepared in a mixing unit 302 located
25 upstream of the reactor 100, wherein water is continuously mixed with the photocatalyst

particles and agitated thoroughly to form the catalyst slurry. In another embodiment, the mixing unit is utilized to store the catalyst slurry and feed the catalyst slurry to the reactor when needed. In a preferred embodiment, the catalyst slurry is maintained in relatively dark conditions in the mixing unit, wherein illuminance in the mixing unit is less than 0.001 lux, preferably less than 0.0001 lux, even more preferably less than 0.00001 lux. The catalyst slurry may be delivered to the internal cavity of the reactor 100 via a first catalyst line 320, which fluidly connects the mixing unit 302 to the reactor 100 via the liquid phase inlet 104, and a first pump 303. In one embodiment, a second catalyst line 322 fluidly connects the reactor 100 to the mixing unit 302 via the liquid phase outlet 106 to discharge used catalyst slurry to the reactor 100 via a second pump 304. In another embodiment, the used catalyst slurry is discharged to a regenerator prior to delivery to the mixing unit, wherein the used catalyst slurry is regenerated. The first and the second pumps may be centrifugal, rotatory, or positive displacement pumps. Additionally, the first and the second catalyst lines may be tubular conduits that are configured to transport a liquid. In one embodiment, the first and the second catalyst lines are substantially similar and are made of a metal or an alloy that are coated with a polymer (e.g. epoxy). In a preferred embodiment, the first and the second catalyst lines are made of a polymeric material.

In addition to the photocatalytic water splitting reactor and the mixing unit, the water splitting system 300 further involves a natural gas source 306 located upstream of the photocatalytic water splitting reactor and is fluidly connected to the gas inlet of the photocatalytic water splitting reactor via a natural gas line.

The natural gas source 306 may be a storage tank or an upstream processing unit (e.g. fluid catalytic cracking, or hydrocracking) that supplies a natural gas to the reactor 100. An auxiliary compressor may be located downstream of the storage tank or the upstream processing unit, and upstream of the reactor 100 to bring the pressure of the natural gas to a

predetermined pressure prior to delivering the natural gas to the reactor 100. In one embodiment, the vessel is made of the transparent material, and the predetermined pressure may be at least 1 bar, preferably at least 2 bars, or preferably at least 3 bars, or preferably at least 4 bars, but no more than 5 bars. In another embodiment, the vessel is made of a metal or
5 a metal alloy, and the predetermined pressure may be at least 5 bars, preferably at least 10 bars, or preferably at least 15 bars, or preferably at least 20 bars, but no more than 30 bars.

The natural gas may be injected to the catalyst slurry via the perforations of the perforated tube 112 to continuously agitate the catalyst slurry. In one embodiment, the natural gas may be injected to the catalyst slurry with a pressure of at least 2 bars, or preferably at
10 least 3 bars, or preferably at least 4 bars, but no more than 5 bars. In one embodiment, agitating the catalyst slurry by the natural gas deagglomerates the photocatalyst particles that are clumped, and/or prevents agglomeration of the photocatalyst particles. In another embodiment, agitating the catalyst slurry by the natural gas provides a larger catalyst surface area, wherein the photocatalysis occurs.

15 Natural gas is a naturally occurring gas mixture, consisting mainly of methane. Natural gas may generally comprise methane, ethane, propane, i-butane, n-butane, nitrogen, carbon dioxide, oxygen, and traces of i-pentane, n-pentane, hexane, and hydrogen. In a preferred embodiment, the natural gas comprises methane and one or more of ethane, carbon dioxide, nitrogen, hydrogen sulfide, and water vapor, wherein the percent volume of methane
20 in the natural gas is at least 90%, preferably at least 92%, or preferably at least 94%, or preferably at least 96%, or preferably at least 98%, or preferably at least 99%. Natural gas can also come from other sources such as by products from a chemical processing unit (e.g. a hydrocracking unit); accordingly, natural gas does not need to come directly from mother earth. In another embodiment, a gaseous mixture may be used instead of the natural gas,
25 wherein the gaseous mixture comprises one or more of argon, helium, methane, ethane,

carbon dioxide, hydrogen sulfide, and preferably nitrogen. The gaseous mixture may preferably be substantially free from oxygen and water vapor.

Oxygen and hydrogen are formed during the photocatalysis of water within the internal cavity of the reactor. In a preferred embodiment, the oxygen and the hydrogen are
5 diluted with the natural gas to avoid reaching an explosive limit (or flammability limit) of oxygen concentration in presence of hydrogen. Explosive limit (or flammability limit) refers to a concentration range of a gas or a vapor in a gaseous mixture (e.g. air) capable of producing a flash of fire in presence of an ignition source (e.g. arc, flame, heat). Lower bound of the concentration range refers to “lower explosive limit” (i.e. lowest concentration of a gas
10 in a gaseous mixture capable of producing a flash of fire in presence of an ignition source), whereas upper bound of the concentration range refers to “upper explosive limit” (i.e. highest concentration of a gas in a gaseous mixture capable of producing a flash of fire in presence of an ignition source). Lower explosive limit and upper explosive limit of oxygen in a gas mixture of oxygen and hydrogen are 4% and 96% by volume, respectively, wherein the
15 natural gas reduces oxygen concentration in the gas mixture to less than 4%, preferably less than 3%, or preferably less than 2%, or preferably less than 1% by volume of oxygen.

Without the addition of natural gas, a product gaseous mixture is formed from the photocatalysis of water, wherein the product gaseous mixture has about 65 – 75%, preferably about 69% by volume of hydrogen, 5 – 10%, preferably about 8.5% by volume of oxygen, 20 – 25%, preferably about 22% by volume of carbon dioxide, and less than 1% by volume of water vapor. In one embodiment, at least 1 m³, preferably at least 5 m³, more preferably at least 10 m³ of the natural gas is injected to the catalyst slurry per 1 liter of the catalyst slurry, wherein the product gaseous mixture has about 25 – 35%, preferably about 30% by volume of methane, 45 – 55%, preferably about 48% by volume of hydrogen, 1 – 10%, preferably
25 about 4% by volume of oxygen, 15 – 20%, preferably about 16% by volume of carbon

dioxide, and less than 0.1% by volume of water vapor. In one embodiment, volumetric concentration of oxygen in the product gaseous mixture after injecting the natural gas is outside the explosive limit of oxygen concentration in the presence of hydrogen.

In one embodiment, the oxygen, the hydrogen, and the natural gas egresses the reactor 5 100 from the gas outlet 110. In another embodiment, the gas outlet is fluidly connected to a perforated conduit, wherein the oxygen, the hydrogen, and the natural gas egresses the reactor through the perforated conduit. In a preferred embodiment, the perforated conduit has a longitudinal axis that is parallel to the longitudinal axis of the vessel and is located proximal to the top of the vessel. In another embodiment, the perforated conduit is located along the 10 side wall of the vessel. The perforated conduit may be rectangular, or preferably cylindrical, which is straight or preferably extended helically along the longitudinal axis of the vessel. In one embodiment, the perforations of the perforated conduit are equally spaced apart around the circumference and along a length of the perforated conduit. The perforations are substantially similar, preferably circular, having a diameter in the range of 1 – 20 mm, 15 preferably 1 – 10 mm, or preferably 5 – 10 mm. The length of the perforated conduit may be at least 5 m, preferably at least 10 m, or preferably at least 15 m, or preferably at least 20 m with respect to the length of the vessel which is in the range of 0.5 – 20 m, preferably 1 – 10 m, or preferably 2 – 10 m, or preferably 3 – 10 m, or preferably 4 – 10 m, or preferably 5 – 10 m. The inner diameter of the perforated conduit may be in the range of 1 – 10 cm, 20 preferably 1 – 5 cm, or preferably 1 – 2 cm with respect to the internal diameter of the gas outlet, and the thickness of the perforated conduit may be in the range of 3 – 50 mm, preferably 5 – 20 mm, more preferably 5 – 10 mm.

In a preferred embodiment, the water splitting system 300 further involves a first gas separation unit 308 located downstream of the reactor 100 and is fluidly connected to the gas 25 outlet 110 of the reactor 100 via product gas lines 323 and 324. In one embodiment, the first

gas separation unit is configured to receive the oxygen, the hydrogen, and the natural gas from the reactor and to separate hydrogen from the oxygen and the natural gas, to form a hydrogen stream and a fuel stream comprising oxygen and the natural gas. Hydrogen concentration in the hydrogen stream may be at least 80%, preferably at least 85%, or
5 preferably at least 90%, or preferably at least 95% by volume of hydrogen. The hydrogen stream may comprise less than 10%, preferably less than 5%, more preferably less than 1% by volume of methane, oxygen, carbon dioxide, nitrogen, hydrogen sulfide, and/or water vapor. The hydrogen stream may further be delivered to a hydroprocessing unit such as a hydrocracker or a hydrotreater (i.e. hydrodesulfurization), an ammonia manufacturing plant,
10 and so forth via a hydrogen gas line 336. The hydrogen stream may also be utilized in hydrogenation units for hydrogenating nitriles, saturation of olefins, hydrogenation of aromatic compounds, hydrogenation of esters to alcohols, and conversion of carbon monoxide to methanol, etc.

In one embodiment, the fuel stream comprises oxygen and methane and one or more
15 of hydrogen, carbon dioxide, nitrogen, hydrogen sulfide, and/or water vapor. In one embodiment, hydrogen concentration in the fuel stream is less than 5%, preferably less than 4%, or preferably less than 3%, or preferably less than 2%, or more preferably less than 1% by volume of hydrogen. In another embodiment, concentration of nitrogen, hydrogen sulfide, and water vapor in the fuel stream is less than 10%, preferably less than 5%, or preferably
20 less than 4%, or preferably less than 3%, or preferably less than 2%, or more preferably less than 1% by volume. In one preferred embodiment, the fuel stream is transported to a power generation plant, or an ammonia manufacturing plant, or a cracker to be used as a fuel. For example, in one embodiment, the fuel stream is delivered to a combustor, which is located downstream of the first gas separation unit and fluidly connected to the first gas separation

unit, wherein the fuel stream is combusted and further rotates turbine blades to generate power.

In another preferred embodiment, the water splitting system 300 further involves a second gas separation unit 310 located downstream of the first gas separation unit 308 and is fluidly connected to the first gas separation unit 308 via a first reflux line 326, whereby the fuel stream is transported. In one embodiment, the second gas separation unit is configured to separate oxygen from the fuel stream to form an oxygen stream and a methane-rich stream. Oxygen concentration in the oxygen stream may be at least 80%, preferably at least 85%, or preferably at least 90%, or preferably at least 95% by volume of oxygen. The oxygen stream preferably comprises less than 10%, or less than 5%, or even less than 1% by volume of hydrogen, methane, carbon dioxide, nitrogen, hydrogen sulfide, and/or water vapor. In one embodiment, the oxygen stream may further be delivered to an oxidation unit (e.g. catalytic partial oxidizing unit, or thermal oxidizer) via an oxygen gas line 334.

The methane-rich stream may preferably comprise less than 10%, or less than 5%, or even less than 1% by volume hydrogen, hydrogen sulfide, and/or water vapor. In one preferred embodiment, the methane-rich stream is recycled to the reactor 100 as the natural gas. According to this embodiment, the methane-rich stream is delivered to a gas mixer 312 via a second reflux line 328, which fluidly connects the second gas separation unit 310 to the gas mixer 312, which is located downstream of the second gas separation unit 310 and upstream of the reactor 100. According to this embodiment, the gas mixer 312 is further connected to the natural gas source 306 via a natural gas line 330. In one embodiment, the methane-rich stream is combined with the natural gas coming from the natural gas source in the gas mixer to form a recycle stream. The recycle stream preferably comprises methane and one or more of ethane, carbon dioxide, nitrogen, hydrogen sulfide, and water vapor, wherein composition of methane is at least 90%, preferably at least 92%, or preferably at least 94%,

or preferably at least 96%, or preferably at least 98%, or preferably at least 99% by volume. In one embodiment, the recycle stream is delivered to the reactor 100 via a third reflux line 332, which fluidly connects the gas mixer 312 to the gas inlet 108 of the reactor 100, and a first compressor 314. In a preferred embodiment, the first compressor 314 is located
5 downstream of the gas mixer and upstream of the reactor to bring the pressure of the recycle stream to the predetermined pressure (i.e. at least 1 bar, preferably at least 2 bars, or preferably at least 3 bars, or preferably at least 4 bars, but no more than 5 bars) prior to delivering to the reactor.

Gas mixer refers to an operational unit that is adapted to mix a plurality of gas
10 streams, preferably at low pressure (i.e. up to 10 bars), and deliver a mixed gas stream, wherein the mixed gas stream contains each of the plurality of gas streams.

The first and the second gas separation units may be pressure swing adsorption units, vacuum swing adsorption units, and/or temperature swing adsorption units, although pressure swing adsorption units are preferred. Other gas separation techniques may also be used,
15 including, but not limited to membrane gas separation, sweep gas membrane distillation, vapor-liquid extraction, cryogenic distillation, and/or any combination thereof.

In one embodiment, the first 326, the second 328, and the third reflux lines 332 as well as the product gas lines 323 and 324, the natural gas line 330, the oxygen gas line 334, and the hydrogen gas line 336 are tubular channels that are configured to transport a gas
20 throughout the water splitting system. In one embodiment, the gas lines are substantially similar and are made of a metal or an alloy that is coated with a polymer (e.g. epoxy), wherein the gas lines are configured to bear a pressure up to 100 bars, preferably up to 200 bars, even more preferably up to 500 bars.

In one embodiment, the water splitting system 300 further involves a second
25 compressor 316 located downstream of the reactor 100 and upstream of the first gas

separation unit 308, and a third compressor 318 located downstream of the first gas separation unit 308 and upstream of the second gas separation unit 310. The first, the second, and the third compressors may be centrifugal, reciprocating, or rotary compressors.

Referring now to Fig. 3A. In one embodiment, Fig 3A is an overview of the water splitting system 300, wherein the natural gas and the catalyst slurry are subjected to the reactor 100 via the lines 330 and 320, respectively, and the product gaseous mixture is transferred to the separation unit 308 via the compressor 316 and the product gas lines 323 and 324 to form the hydrogen stream and the fuel stream to be further transported to downstream processing units via the lines 336 and 326, respectively.

According to a third aspect the present disclosure relates to a method of photocatalytic water splitting, involving exposing the liquid phase within the internal cavity of the photocatalytic water splitting reactor to the light source (e.g. visible light, UV light), while concurrently agitating the liquid phase with the natural gas from the natural gas source (or the recycle stream from the gas mixer) to dissociate water to form hydrogen and oxygen. The liquid phase as used herein refers to the catalyst slurry. In a preferred embodiment, the reactor is oriented such that exposure surface area (i.e. surface area of the catalyst slurry which is in direct contact with photons from the light source) is maximized. Accordingly, the preferred orientation is when the reactor is horizontally oriented.

The method of photocatalytic water splitting further involves collecting the hydrogen, the oxygen, and the natural gas.

In one embodiment, the method of photocatalytic water splitting further involves separating the hydrogen in the first gas separation unit to form the hydrogen stream and the fuel stream comprising the oxygen and the natural gas. The hydrogen stream may further be transferred to a hydroprocessing unit such as a hydrocracker or a hydrotreater (i.e. hydrodesulfurization), or an ammonia manufacturing plant, whereas the fuel stream is

transported to a power generation plant, an ammonia manufacturing plant, and/or a cracker to be used as a fuel.

In one embodiment, the method of photocatalytic water splitting further involves separating the oxygen from the fuel stream in the second gas separation unit to form the
5 oxygen stream and the methane-rich stream, wherein the oxygen stream may be delivered to an oxidation unit.

In one embodiment, the method of photocatalytic water splitting further involves mixing the methane-rich stream and the natural gas in the gas mixer to form the recycle stream, and delivering the recycle stream to the reactor.

10 The examples below are intended to further illustrate protocols for the photocatalytic water splitting and are not intended to limit the scope of the claims.

EXAMPLE

Two methods were developed where photocatalytic water splitting was carried out
15 with and without the use of sacrificial agents (such as glycerol). For the catalysts that required the presence of a sacrificial agent, hydrogen yield was improved, and a portion of oxygen was converted to carbon-dioxide. For the catalysts that did not require the presence of a sacrificial agent, hydrogen and oxygen were produced in a stoichiometric ratio. In both cases, the hydrogen and oxygen were co-produced around catalyst particles.

20 There are two challenges when using photocatalytic water splitting approach toward hydrogen production. The first one is that the particles easily agglomerate to sizes larger than 100 micrometers and precipitate in the catalyst slurry. This phenomenon reduces the effective surface area of the photocatalyst particles and thus decreasing the hydrogen production yield. The second challenge is the safety issue dealing with producing hydrogen and oxygen in the
25 same chamber. In the case when a sacrificial agent is used, the amount of oxygen is lower

than the case when a sacrificial agent is not used. However, in both cases, the formation of gas mixtures that have amounts of oxygen and hydrogen that are within the explosive limit needs to be hindered. The explosive limit of an oxygen gas in a hydrogen gas is in the range of 4% to 96 % by volume of oxygen to the total volume.

5 The first challenge of agglomeration and sedimentation of the catalysts was solved by continuously bubbling a natural gas (e.g. methane) through the reactor from perforations of a tube inside the reactor. The second challenge of reducing the risk associated with generating a flammable mixture of oxygen and hydrogen was resolved by varying the amount of the natural gas to keep the content of the produced oxygen outside the explosive limit. The
10 amount of the natural gas needed to dilute the mixture of oxygen and hydrogen is a function of the type of the photocatalyst and the sacrificial agent used. Initial evaluations showed that bubbling a natural gas can effectively agitate the catalyst slurry and prevent photocatalyst particles from agglomeration and sedimentation, and also keep the produced gas mixture outside the explosive limit.

15 The process as shown in Figure 3B was simulated for a photocatalytic hydrogen production plant using AspenPlus with key assumptions and reactor design parameters as given in Table 1. The simulation also used a reduced amount of sacrificial agent at 10% glycerol to oxygen stoichiometric ratio, while suppressed the reactor off gas oxygen concentration to a safe level of 4 vol% by a natural gas sweep. The slurry solid concentration
20 was held at an optimum level of 0.1 wt%. The residence time of the gas phase in the photocatalytic reactor was calculated to be 1.2 hour, and the liquid was held for 3757 hours.

Table 1. Design parameters of the photocatalytic water splitting reactor, and simulation parameters of the process flow diagram of Figure 3B.

PCWS 350 ton/day H2 Plant	Unit	4%O2 CH4 Case
<u>Design Parameter</u>		
Solar Ray Power	w/m ² /hr sunshine	1000
STH (solar-to-hydrogen)	%	4%
H2 LHV	kwh/kg	33.32
Device Efficiency	%	40%
Unit H2 productivity	gm H2/gm cat/hr	0.48
Unit H2 productivity	gmole H2/gm cat/min	0.004001
<u>Target by Simulation</u>		
H2 Production	ton/day	350
	kmol/hr	7233
Reactor Offgas O2	mol%	4.00%
Catalysts	ton	112
Slurry Rxt Volume @50% gas holdup	m ³	2242617
<u>Results by Simulation</u>		
Water Feed	kg/hr	177993
	liter/min	2999
Glycerol Feed	kg/hr	9613
	liter/min	126
NG Feed	kg/hr	500795
	liter/min	2452480
Reactor Gas Effluent (108)	kg/hr	1340670
	liter/min	31515300
H2	mol%	0.00%
H2O	mol%	0.00%
O2	mol%	
CO2	mol%	0.00%
CH4	mol%	0.00%
Reactor Internal Slurry Recycle (322)	kg/hr	200000
	liter/min	3479
Water	wt%	99.88%
CO2	wt%	0.02%
Titan Oxide Catalyst	wt%	0.10%
GHSV	liter/liter Rxt/hr	0.843
Rxt Gas Residence time	Hrs	1.19
LHSV	liter/liter Rxt/hr	0.000266
Rxt Liquid Residence time	Hrs	3756.64

Table 2. Simulation results of a hydrogen production plant as shown in the process flow diagram of Figure 3B, with a production rate of 350 ton/day.

Stream on Fig 3B	323	320	322	324	326	328	330	332	334	336
Mole Flow kmol/hr										
H ₂ O	13741.46	9880.093	11088.31	3063.72	3063.413	0.306341	0	0.306341	3063.107	0.306372
H ₂	7306.634	0	0.015476	7306.565	73.06565	72.33499	0	72.33499	0.730657	7233.499
O ₂	3284.335	0	8.37E-03	3284.298	3251.455	32.51455	0	32.51455	3218.94	32.84298
N ₂	446.4643	0	6.32E-04	446.4615	441.9969	4.419969	442.0416	446.4615	437.5769	4.464615
CO ₂	349.0894	0	0.706284	346.0588	344.3286	3.443286	29.46944	32.91272	340.8853	1.730294
CH ₄	55127.54	0	0.142791	55126.91	54851.27	27425.64	27701.27	55126.91	27425.64	275.6345
C ₃ H ₈ O ₃	0	104.3805	0	0	0	0	0	0	0	0
C ₂ H ₆	1473.662	0	0.191737	1472.841	1471.368	441.4103	1031.43	1472.841	1029.957	1.472841
C ₃ H ₈	378.9165	0	0.035924	378.7629	378.4599	113.538	265.2249	378.7629	264.9219	0.30301
TITAN-01	2.52E-78	0	2.503793	0	0	0	0	0	0	0
Mole Frac										
H ₂ O	0.167358	0.989546	0.999675	0.042894	0.047959	1.09E-05	0	5.32E-06	0.085605	4.06E-05
H ₂	0.088988	0	1.40E-06	0.102296	1.14E-03	2.57E-03	0	1.26E-03	2.04E-05	0.958047
O ₂	0.04	0	7.54E-07	0.045982	0.050903	1.16E-03	0	5.65E-04	0.08996	4.35E-03
N ₂	5.44E-03	0	5.69E-08	6.25E-03	6.92E-03	1.57E-04	0.015	7.76E-03	0.012229	5.91E-04
CO ₂	4.25E-03	0	6.37E-05	4.85E-03	5.39E-03	1.23E-04	1.00E-03	5.72E-04	9.53E-03	2.29E-04
CH ₄	0.671402	0	1.29E-05	0.771809	0.858724	0.976224	0.94	0.957679	0.76647	0.036507
C ₃ H ₈ O ₃	0	0.010454	0	0	0	0	0	0	0	0
C ₂ H ₆	0.017948	0	1.73E-05	0.020621	0.023035	0.015712	0.035	0.025587	0.028784	1.95E-04
C ₃ H ₈	4.61E-03	0	3.24E-06	5.30E-03	5.92E-03	4.04E-03	9.00E-03	6.58E-03	7.40E-03	4.01E-05
TITAN-01	3.07E-83	0	2.26E-04	0	0	0	0	0	0	0
Mass Flow kg/hr										
H ₂ O	2.48E+05	1.78E+05	2.00E+05	55193.77	55188.25	5.518825	0	5.518825	55182.73	5.519377
H ₂	14729.3	0	0.031198	14729.16	147.2916	145.8187	0	145.8187	1.472916	14581.87
O ₂	1.05E+05	0	0.267697	1.05E+05	1.04E+05	1040.427	0	1040.427	1.03E+05	1050.936
N ₂	12507.02	0	0.017692	12506.94	12381.87	123.8187	12383.12	12506.94	12258.05	125.0694
CO ₂	15363.36	0	31.08341	15229.98	15153.83	151.5383	1296.944	1448.482	15002.29	76.1499
CH ₄	8.84E+05	0	2.29076	8.84E+05	8.80E+05	4.40E+05	4.44E+05	8.84E+05	4.40E+05	4421.939
C ₃ H ₈ O ₃	0	9612.892	0	0	0	0	0	0	0	0
C ₂ H ₆	44312.49	0	5.765453	44287.79	44243.5	13273.05	31014.74	44287.79	30970.45	44.28779
C ₃ H ₈	16708.9	0	1.584104	16702.13	16688.75	5006.629	11695.5	16702.13	11682.13	13.3617
TITAN-01	2.01E-75	0	200	0	0	0	0	0	0	0
Mass Frac										
H ₂ O	0.184651	0.94876	0.998795	0.048073	0.048934	1.20E-05	0	5.75E-06	0.082599	2.72E-04
H ₂	0.010987	0	1.56E-07	0.012829	1.31E-04	3.17E-04	0	1.52E-04	2.20E-06	0.717642
O ₂	0.07839	0	1.34E-06	0.091534	0.092252	2.26E-03	0	1.08E-03	0.154176	0.051722
N ₂	9.33E-03	0	8.85E-08	0.010893	0.010979	2.69E-04	0.024727	0.013021	0.018348	6.16E-03
CO ₂	0.011459	0	1.55E-04	0.013265	0.013436	3.30E-04	2.59E-03	1.51E-03	0.022456	3.75E-03
CH ₄	0.659669	0	1.15E-05	0.770285	0.780242	0.957047	0.887399	0.920734	0.658576	0.217624
C ₃ H ₈ O ₃	0	0.05124	0	0	0	0	0	0	0	0
C ₂ H ₆	0.033052	0	2.88E-05	0.038574	0.03923	0.028871	0.061931	0.046108	0.046357	2.18E-03
C ₃ H ₈	0.012463	0	7.92E-06	0.014547	0.014797	0.01089	0.023354	0.017389	0.017486	6.58E-04
TITAN-01	1.50E-82	0	1.00E-03	0	0	0	0	0	0	0
Total Flow kmol/hr	82108.1	9984.474	11091.91	71425.61	63875.36	28093.6	29469.44	57563.04	35781.76	7550.254
Total Flow kg/hr	1.34E+06	1.88E+05	2.00E+05	1.15E+06	1.13E+06	4.60E+05	5.01E+05	9.61E+05	6.58E+05	20319.13
Total Flow l/min	3.15E+07	3119.574	3479.475	6.83E+06	8.62E+06	1.58E+07	2.45E+06	1.81E+07	2.01E+07	2.90E+06
Temperature C	60	29.54247	60	60	214.1964	213.5944	30	181.215	213.5944	58.77793
Pressure bar	1.2	5	1.2	4.8	5	1.2	5	2	1.2	1.2
Density gm/cc	7.09E-04	1.002303	0.957999	2.80E-03	2.18E-03	4.85E-04	3.40E-03	8.84E-04	5.54E-04	1.17E-04
Average MW	16.32811	18.78973	18.03116	16.0745	17.65645	16.36421	16.99371	16.68649	18.67103	2.691185

CLAIMS

Claim 1: A photocatalytic water splitting reactor, comprising:

a horizontally oriented vessel with a first and a second end separated by a side wall along a longitudinal axis of the vessel and an internal cavity configured to hold a liquid phase proximal to the bottom of the vessel and a gas phase proximal to the top of the vessel;

a liquid phase inlet and a first valve attached to the liquid phase inlet located proximal to the bottom of the vessel;

a liquid phase outlet and a second valve attached to the liquid phase outlet located proximal to the bottom of the vessel;

a gas inlet and a third valve attached to the gas inlet located proximal to the bottom of the vessel;

a perforated tube fluidly connected to the gas inlet, wherein the perforated tube has a longitudinal axis that is parallel to the longitudinal axis of the vessel and is located proximal to the bottom of the vessel;

a gas outlet and a fourth valve attached to the gas outlet located proximal to the top of the vessel;

wherein the liquid phase inlet and the liquid phase outlet are adapted for loading and unloading the vessel with the liquid phase,

and wherein the perforated tube is configured to disperse the gas phase into the liquid phase.

Claim 2: The reactor of claim 1, wherein the perforated tube is straight and located along the side wall of the vessel.

Claim 3: The reactor of claim 1, wherein the perforated tube is helically extended along the longitudinal axis of the vessel.

Claim 4: The reactor of claim 1, wherein the perforated tube has perforations that are equally spaced apart around the circumference and along a length of the perforated tube.

Claim 5: The reactor of claim 1, wherein the liquid phase inlet, the liquid phase outlet, and the gas inlet are located on the first end of the vessel.

Claim 6: The reactor of claim 1, further comprising:
a light source located inside the vessel and is configured to be submerged in the liquid phase, wherein the light source generates visible light and/or UV light.

Claim 7: The reactor of claim 6, wherein the light source is in the form of an elongated structure that has a longitudinal axis which is parallel to the longitudinal axis of the vessel.

Claim 8: The reactor of claim 1, wherein the vessel is made of a transparent material to expose the internal cavity to sunlight.

Claim 9: The reactor of claim 1, further comprising:
a heating/cooling jacket which covers a portion of an external surface of the vessel.

Claim 10: A water splitting system, comprising:
the photocatalytic water splitting reactor of claim 1; and

a natural gas source located upstream of and fluidly connected to the gas inlet of the photocatalytic water splitting reactor via a natural gas line, wherein the natural gas source supplies a natural gas to the photocatalytic water splitting reactor to agitate the liquid phase, which comprises water and a photocatalyst, to dissociate water in presence of the photocatalyst to form hydrogen and oxygen.

Claim 11: The system of claim 10, further comprising:

a first gas separation unit located downstream of and fluidly connected to the gas outlet of the photocatalytic water splitting reactor via a product gas line, wherein the first gas separation unit is configured to receive the oxygen, the hydrogen, and the natural gas from the photocatalytic water splitting reactor and to remove hydrogen to form a hydrogen stream and a fuel stream comprising oxygen and the natural gas.

Claim 12: The system of claim 11, further comprising:

a second gas separation unit located downstream of and fluidly connected to the first gas separation unit via a first reflux line, wherein the second gas separation unit is configured to remove oxygen from the fuel stream to form an oxygen stream and a methane-rich stream.

Claim 13: The system of claim 11, further comprising:

a combustor located downstream of and fluidly connected to the first gas separation unit, wherein the fuel stream is combusted.

Claim 14: The system of claim 12, further comprising:

a second reflux line which fluidly connects the second gas separation unit to a gas mixer, which is located downstream of the second gas separation unit and upstream of the

photocatalytic water splitting reactor, wherein the second reflux line delivers the methane-rich stream to the gas mixer, wherein the methane-rich stream is combined with the natural gas to form a recycle stream; and

a third reflux line which fluidly connects the gas mixer to the gas inlet of the photocatalytic water splitting reactor, wherein the third reflux line delivers the recycle stream to the photocatalytic water splitting reactor.

Claim 15: The system of claim 10, further comprising:

a light source which is located inside the photocatalytic water splitting reactor and is configured to be submerged in the liquid phase.

Claim 16: The system of claim 12, wherein the first and the second gas separation units are pressure swing adsorption units.

Claim 17: The system of claim 10, wherein the natural gas comprises methane and one or more of ethane, carbon dioxide, nitrogen, and hydrogen sulfide.

Claim 18: A method of photocatalytic water splitting, comprising:

exposing a liquid phase comprising water and a photocatalyst to visible light and/or UV light within an internal cavity of a photocatalytic water splitting reactor while concurrently agitating the liquid phase with a natural gas to dissociate water to form hydrogen and oxygen;

collecting the hydrogen, the oxygen, and the natural gas; and

separating the hydrogen in a first gas separation unit to form a hydrogen stream and a fuel stream comprising the oxygen and the natural gas.

Claim 19: The method of claim 18, further comprising:

removing the oxygen from the fuel stream in a second gas separation unit to form an oxygen stream and a methane-rich stream;

mixing the methane-rich stream and the natural gas in a gas mixer to form a recycle stream; and

delivering the recycle stream to the photocatalytic water splitting reactor.

Claim 20: The method of claim 18, further comprising:

delivering the hydrogen stream to a hydroprocessing and/or hydrotreating unit; and

delivering the fuel stream to a power generation plant and/or ammonia production plant.

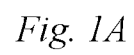
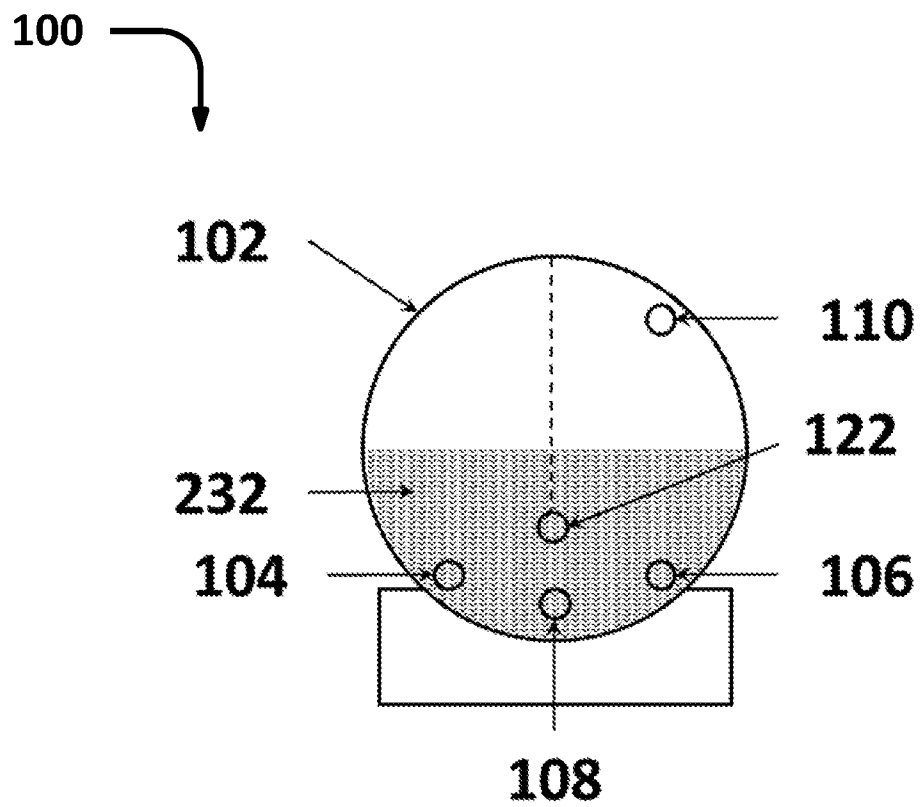
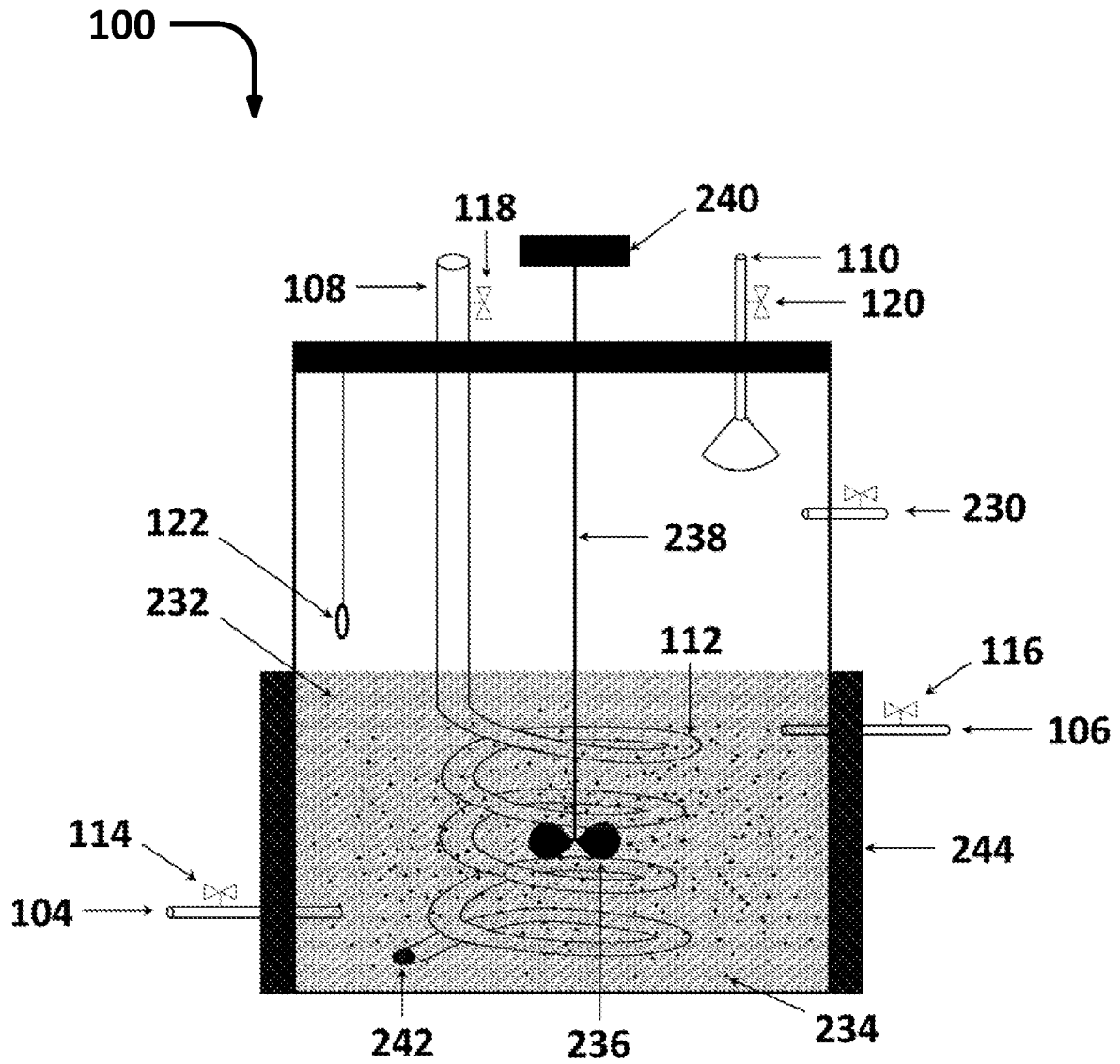
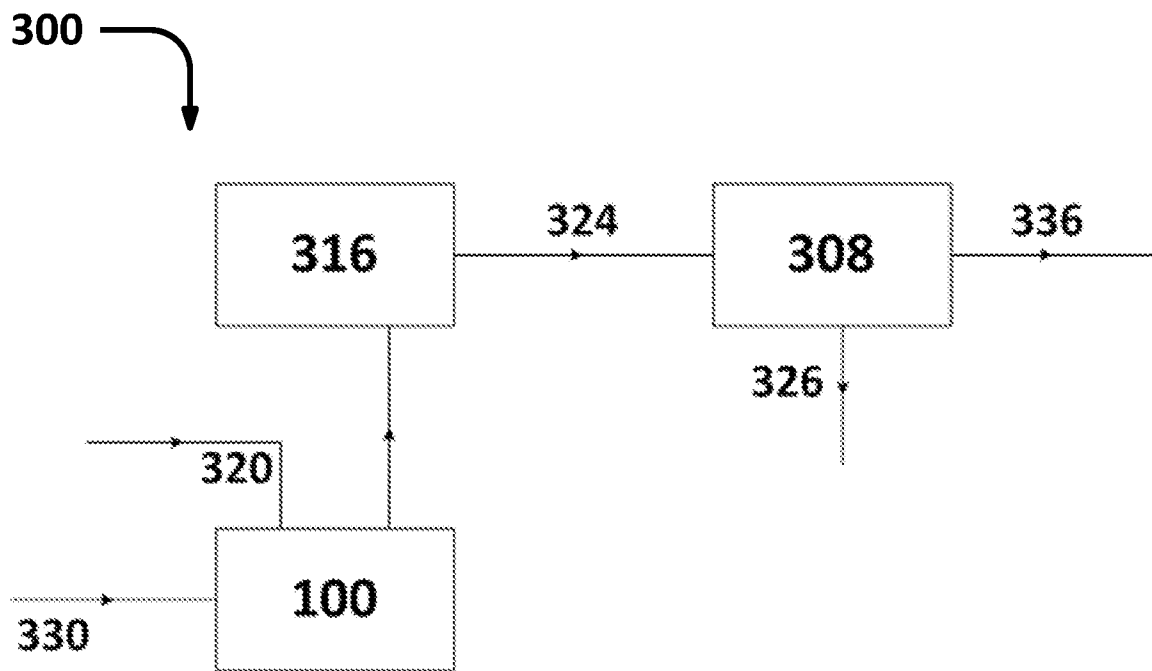


Fig. 1A

*Fig. 1B*

*Fig. 2*

*Fig. 3A*

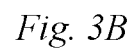


Fig. 3B

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/036145

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B3/04 C01B13/02 C01B3/56 C01B3/50
ADD.

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)

C01B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/035919 A2 (SUN CATALYTIX CORP [US]) 6 March 2014 (2014-03-06)	1,2,5,8
A	paragraphs [0027] - [0051]; figures 2,3 claims	9-20
X	----- CN 104 760 932 A (SHUIMUQINGYUAN TIANJIN ENERGY ENVIRONMENT TECHNOLOGY CO LTD) 8 July 2015 (2015-07-08)	1,2,5-7
A	abstract; figure	3,4,8
A	----- CN 102 671 597 A (UNIV HENAN SCIENCE & TECH) 19 September 2012 (2012-09-19)	1-9
	abstract; figure	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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Date of the actual completion of the international search

8 August 2017

Date of mailing of the international search report

17/08/2017

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/036145

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014035919	A2	06-03-2014	NONE
CN 104760932	A	08-07-2015	NONE
CN 102671597	A	19-09-2012	NONE