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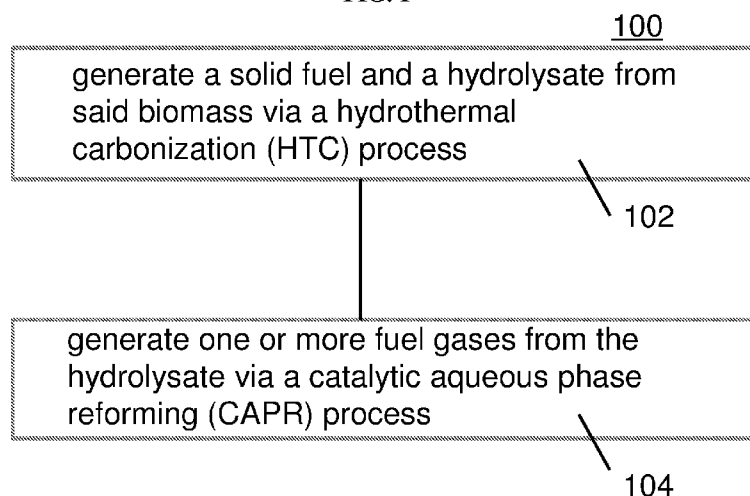
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FIG. 1



(57) Abstract: Provision of a method for converting biomass to fuel gas comprising a first step of generating a solid fuel, a hydrolysate and a gas via hydrothermal carbonization (HTC) of the said biomass, and a second step of subjecting the hydrolysate to catalytic aqueous phase reforming (CAPR) to generate the fuel gas. The fuel gases are preferably selected from methane or hydrogen.

METHOD AND SYSTEM FOR CONVERTING BIOMASS TO FUEL PRODUCTS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10201504349U filed on June 3, 2015, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various aspects of this disclosure relate to methods and systems for converting biomass to fuel products.

BACKGROUND

[0003] Due to the high moisture content of wet biomass waste streams, conventional thermochemical conversion of these wastes could be energy-intensive as prior drying is required.

SUMMARY

[0004] Various aspects of this disclosure provide a method for converting biomass to fuel products. The method may include generating a solid fuel and a hydrolysate from said biomass via a hydrothermal carbonization (HTC) process. The method may further include generating one or more fuel gases from the hydrolysate via a catalytic aqueous phase reforming (CAPR) process.

[0005] Various aspects of this disclosure provide a system for converting biomass to fuel products according to various embodiments. The system may include a first stage configured to generate a solid fuel and hydrolysate from said biomass. The system may include a second stage configured to generate one or more fuel gases from the hydrolysate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

FIG. 1 is a schematic illustrating a method for converting biomass to fuel products according to various embodiments.

FIG. 2 is a schematic illustrating a system for converting biomass to fuel products according to various embodiments.

FIG. 3 is a schematic illustrating a method for converting biomass to fuel products according to various embodiments.

FIG. 4 is a table showing the gas composition and yield during catalytic aqueous phase reforming of hydrolysate derived from hydrothermal carbonization of cellulose according to various embodiments.

FIG. 5 is an image showing a reactor used for hydrothermal carbonization (HTC) according to various embodiments.

FIG. 6 is a graph showing the moisture content and ash content for raw sewage sludge and hydrochars after hydrothermal carbonization under different residence time according to various embodiments.

FIG. 7A is an image showing containers with ash residue from raw sewage sludge, ash residue from hydrochar obtained after 4 hours of hydrothermal carbonization, and ash residue from hydrochar obtained after 6 hours of hydrothermal carbonization according to various embodiments.

FIG. 7B is an image showing ash residue from raw sewage sludge, ash residue from hydrochar obtained after 4 hours of hydrothermal carbonization, and ash residue from hydrochar obtained after 6 hours of hydrothermal carbonization.

FIG. 8 is an image of pellets of raw sewage sludge, pellets of hydrochar obtained after 4 hours of hydrothermal carbonization, and pellets of hydrochar obtained after 6 hours of hydrothermal carbonization according to various embodiments.

FIG. 9 is a plot of higher heating value (megajoule per kilogram or MJ/kg) of raw sewage sludge, hydrochar obtained after 4 hours of hydrothermal carbonization, and hydrochar obtained after 6 hours of hydrothermal carbonization according to various embodiments on dry basis (DB) and on dry- and ash-free basis (DAF).

FIG. 10 is a plot of solid hydrochar yield (percent or %) after hydrothermal carbonization under different residence time (i.e. 4 hours and 6 hours), and the chemical oxygen demand (COD) (gram per liter or g/L) for the corresponding aqueous phases according to various embodiments.

FIG. 11 is an image of the aqueous phases obtained after 4 hours of hydrothermal carbonization and after 6 hours of hydrothermal carbonization according to various embodiments.

DETAILED DESCRIPTION

[0007] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, and logical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0008] More recently, hydrothermal technology has been widely employed to convert wet biomass wastes to biofuels in hot-compressed water and it presents significant advantages over thermal drying since water can act as both reactant and solvent during hydrothermal reactions. Generally, the energy content of wet biomass can be densified via dehydration and decarboxylation reactions through hydrothermal carbonization (HTC) under low temperature and pressure and hydrochar solid fuel may be recovered thereafter. In supercritical water, hydrogen- and methane-rich fuel gas may be generated from wet biomass via intense free-radical reactions. Therefore, in various embodiments, hydrothermal conversion may be applied to wet biomass waste streams to efficiently realize simultaneous waste reduction and energy recovery.

[0009] To make the hydrothermal conversion effective and economical in industrial applications, a minimum solid content of 15 weight percent (wt. %) is desired. In the preliminary experiments, a 182 g cellulose solution feedstock with 85 wt. % moisture content was prepared and fed into a 1.0 L autoclave (Parr Instrument Co.) for hydrothermal gasification in near-critical water for 20 min at 380 °C and 22.0 MPa. After reaction, it was found that severe carbonization occurred with significant carbon dioxide (CO₂) production. The overall solid yield was about 40%. As a result of the high solid content (15 weight percent or wt. %) in the cellulose feedstock, carbonization reaction is favored and catalysts could also be deactivated because of deposits of carbonaceous intermediates.

[0010] Various embodiments may seek to address or mitigate some of the above described issues.

[0011] FIG. 1 is a schematic illustrating a method 100 for converting biomass to fuel products according to various embodiments. The method 100 may include, in 102, generating a solid fuel and a hydrolysate from said biomass via a hydrothermal carbonization (HTC) process. The method 100 may further include, in 104, generating one or more fuel gases from the hydrolysate via a catalytic aqueous phase reforming (CAPR) process.

[0012] In other words, the method 100 may be a two-step process including a hydrothermal carbonization step to generate a solid fuel and a hydrolysate, followed by a catalytic aqueous phase reforming step to generate one or more fuel gases from the hydrolysate.

[0013] In various embodiments, the one or more fuel gases may include hydrogen (H_2) gas. In various embodiments, the one or more fuel gases may include alkanes such as methane (CH_4).

[0014] The solid fuel may be referred to as hydrochar, or a solid phase, or a solid portion. Hydrochar may be a solid enriched in carbon, and may have chemical characteristics comparable to fossil fuels.

[0015] The hydrolysate may also be referred to as an aqueous phase, or a liquid portion.

[0016] Hydrothermal carbonization (HTC) is a thermochemical process used for conversion of biomass matter feedstocks into carbonaceous product under elevated temperature and pressure in the presence of water. The resulting products may include solid, liquid, and gas. Particularly, the solid and liquid fractions could be easily separated due to significantly improved dewaterability of original wet biomass streams after HTC, while carbon dioxide is the predominant gas product. HTC may greatly enhance solid fuel quality (e.g. increased carbon content, higher calorific value/energy density and fuel ratio) of raw biomass material and generate cleaner hydrochar solid fuel via two major reaction pathways (i.e. dehydration and decarboxylation). As HTC takes place in an aqueous reaction medium, wet biomass may be used, and may even be preferred. HTC may not require a pre-drying process and may thus be more energy-efficient compared to other thermochemical techniques, such as combustion, gasification, pyrolysis, etc.

[0017] Catalytic aqueous phase reforming (CAPR) is a thermochemical process used to reform aqueous oxygenated hydrocarbons derived from biomass under moderate

temperatures and pressures in the presence of catalysts. CAPR may include dehydrogenation of oxygenated hydrocarbon to produce hydrogen. The oxygenated hydrocarbon may also undergo C-C bond cleavage via decarbonylation and decarboxylation to release carbon monoxide (CO) and carbon dioxide (CO₂), respectively. The CO may consecutively react with water therein through water-gas shift reaction to produce more hydrogen (H₂). On the other hand, cleavage of C-O bond via dehydration of the feedstock and subsequent hydrogenation of dehydrated intermediates using H₂ produced in the first reaction route may also occur. Consecutive cycles of dehydration/hydrogenation may lead to alcohols and alkanes. Additionally, more methane (CH₄) could be generated via methanation during gaseous products interconversion. Generally, CH₄, H₂, CO and CO₂ could be produced from aqueous oxygenated hydrocarbons after CAPR.

[0018] By combining HTC and CAPR processes, a less energy-intensive thermochemical process may be provided to convert wet biomass streams into energy carriers (e.g. solid fuel, H₂- and CH₄-rich fuel gas) via a more sustainable way. Various embodiments may be suitable for processing wet biomass. Various embodiments may increase efficiency of energy production from biomass.

[0019] The biomass may have a solid content selected from a range of about 5 weight percent (wt. %) to about 50 weight percent (wt. %).

[0020] The biomass may be selected from a group consisting of food waste, sewage sludge, algae, animal manure, human waste, horticulture waste, fruit peels, bagasse, winery waste, distilled grains, corn stalks, rice husks, aquatic plants, terrestrial plants, arid land plants, and any combination or mixture thereof.

[0021] In various embodiments, the hydrothermal carbonization process may be carried at a temperature selected from a range of about 150 °C to about 300 °C, e.g. about 180 °C to about 250 °C.

[0022] In various embodiments, the hydrothermal carbonization process may be carried out at a pressure selected from a range of about 10 bars to about 150 bars, e.g. about 20 bars to about 100 bars.

[0023] In various embodiments, the hydrothermal carbonization process may be carried out for a duration selected from about 1 hour to about 24 hours.

[0024] The method may further include separating the solid fuel and hydrolysate, e.g. by using a separator. The separation may be carried out after HTC, but before CAPR.

[0025] In various embodiments, the hydrolysate may include hydrocarbons such as sugars and derivatives, organic acids, phenolic compounds, etc. HTC may further generate carbon dioxide gas, and water.

[0026] In various embodiments, the catalytic aqueous phase reforming process may be carried out at a temperature selected from a range of about 150 °C to about 400 °C, e.g. about 200 °C to about 350 °C.

[0027] In various embodiments, the catalytic aqueous phase reforming process may be carried out at a pressure selected from a range of about 10 bars to about 200 bars, e.g. about 30 bars to about 150 bars.

[0028] In various embodiments, the catalytic aqueous phase reforming process may be carried out for a duration selected from about 1 hour to about 12 hours.

[0029] The catalytic aqueous phase reforming process may be carried out in the presence of a catalyst. The catalyst may be a metal catalyst, for instance a noble metal catalyst. The metal catalyst may be selected from a group consisting of ruthenium (Ru), platinum (Pt), palladium (Pd), and any combination or mixture thereof. In various embodiments, the metal catalyst may be an alloy.

[0030] The catalyst may be on a suitable support including a suitable material selected from a group consisting of carbon (C), aluminum oxide (Al₂O₃), titanium oxide (TiO₂), zirconium oxide (ZrO₂), and cerium oxide (CeO₂). In various embodiments, the metal catalyst may be supported on a carbon support. The carbon support may be selected from a group consisting of activated carbon, single-walled carbon nanotubes, multi-walled carbon nanotubes, graphene, and any combination or mixture thereof.

[0031] In various embodiments, the catalytic aqueous phase reforming process may be carried out in the presence of the catalyst with a suitable promotor to facilitate H₂ and/or CH₄ production. The catalyst may be a metal catalyst, such as a transition metal catalyst. In various embodiments, the catalytic aqueous phase reforming process may be carried out in the presence of the catalyst with a base and/or promoter. The suitable promotor may be selected from a group consisting of nickel (Ni), cobalt (Co), rhodium (Rh), copper (Cu), iron (Fe), magnesium (Mg), potassium (K), calcium (Ca), sodium (Na), and caesium (Cs).

[0032] In various embodiments, alkali additives may be used to enhance the yield and/or purity of H₂. The catalytic aqueous phase reforming process may be carried out in the presence of the catalyst with a suitable additive selected from a group consisting of calcium

oxide (CaO), calcium hydroxide (Ca(OH)₂), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium bicarbonate (NaHCO₃), potassium bicarbonate (KHCO₃), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), and any combination or mixture thereof. Natural materials containing any of the additives, e.g. Trona, may also be effective in promoting the yield and/or purity of H₂.

[0033] In various embodiments, catalytic aqueous phase reforming (CAPR) may also produce carbon dioxide gas. In various embodiments, the ratio of the volume of hydrogen gas and methane to the total volume of gases generated (i.e. total volume of hydrogen gas, methane, and carbon dioxide gas produced) may be more than 0.4, or more than 0.45, or more than 0.47.

[0034] In various embodiments, the fuel products may include the solid fuel, and the one or more fuel gases.

[0035] FIG. 2 is a schematic illustrating a system 200 for converting biomass to fuel products according to various embodiments. The system 200 may include a first stage 202 configured to generate a solid fuel and hydrolysate from said biomass. The system 200 may include a second stage 204 configured to generate one or more fuel gases from the hydrolysate.

[0036] In other words, the system 200 may include a portion for producing a solid fuel. The system 200 may further include a portion in which the hydrolysate is used to produce fuel gases.

[0037] In various embodiments, the first stage 202 may be configured to generate the solid fuel and the hydrolysate from said biomass via a hydrothermal carbonization (HTC) process.

[0038] In various embodiments, the second stage 204 may be configured to generate the one or more fuel gases via a catalytic aqueous phase reforming (CAPR) process.

[0039] In various embodiments, the first stage is in a first reactor, and the second stage is in a second reactor. In various other embodiments, the first stage 202 and the second stage 204 may be in one reactor.

[0040] In various embodiments, the system 200 may have an inlet for receiving biomass. In various embodiments, the system 200 may include one or more outlets for outputting the solid fuel, and the one or more fuel gases.

[0041] The one or more fuel gases may include hydrogen (H₂) gas. The one or more fuel gases may include alkanes such as methane (CH₄).

[0042] The biomass may have a solid content selected from a range of about 5 weight percent (wt %) to about 50 weight percent (wt %).

[0043] In various embodiments, the hydrothermal carbonization process may be carried out at a temperature selected from a range of about 150 °C to about 300 °C, e.g. about 180 °C to about 250 °C.

[0044] In various embodiments, the hydrothermal carbonization process may be carried out at a pressure selected from a range of about 10 bars to about 150 bars, e.g. about 20 bars to about 100 bars.

[0045] In various embodiments, the catalytic aqueous phase reforming process may be carried out at a temperature selected from a range of about 150 °C to about 400 °C, e.g. about 200 °C to about 350 °C.

[0046] In various embodiments, the catalytic aqueous phase reforming process may be carried out at a pressure selected from a range of about 10 bars to about 200 bars, about 30 bars to about 150 bars.

[0047] The catalytic aqueous phase reforming process may be carried out in the presence of a catalyst. The catalyst may be a metal catalyst such as a noble metal catalyst. The metal catalyst may be selected from a group consisting of ruthenium (Ru), platinum (Pt), palladium (Pd), and any combination or mixture thereof. The catalyst may be on a suitable support including a suitable material selected from a group consisting of carbon (C), aluminum oxide (Al₂O₃), titanium oxide (TiO₂), zirconium oxide (ZrO₂), and cerium oxide (CeO₂). In various embodiments, the metal catalyst may be supported on a carbon support. The carbon support may be selected from a group consisting of activated carbon, single-walled carbon nanotubes, multi-walled carbon nanotubes, graphene, and any combination or mixture thereof.

[0048] In various embodiments, the catalytic aqueous phase reforming process may be carried out in the presence of the catalyst with a suitable promoter to facilitate H₂ and/or CH₄ production. The catalyst may be a metal catalyst, such as a transition metal catalyst. In various embodiments, the catalytic aqueous phase reforming process may be carried out in the presence of the catalyst with a base and/or promoter. The suitable promoter may be selected from a group consisting of nickel (Ni), cobalt (Co), rhodium (Rh), copper (Cu), iron (Fe), magnesium (Mg), potassium (K), calcium (Ca), sodium (Na), and caesium (Cs).

[0049] In various embodiments, alkali additives may be used to enhance the yield and/or purity of H₂. The catalytic aqueous phase reforming process may be carried out in the

presence of the catalyst with a suitable additive selected from a group consisting of calcium oxide (CaO), calcium hydroxide (Ca(OH)₂), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium bicarbonate (NaHCO₃), potassium bicarbonate (KHCO₃), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), and any combinations or mixtures thereof. Natural materials containing any of the additives, e.g. Trona, may also be effective in promoting the yield and/or purity of H₂.

[0050] The biomass may be selected from a group consisting of food waste, sewage sludge, algae, animal manure, human waste, horticulture waste, fruit peels, bagasse, winery waste, distilled grains, corn stalks, rice husks, aquatic plants, terrestrial plants, arid land plants, and any combination or mixture thereof.

[0051] **Example 1**

[0052] FIG. 3 is a schematic illustrating a method 300 for converting biomass 306 to fuel products 308, 312 according to various embodiments. In the first stage 302, wet biomass waste 306 may be converted to hydrochar solid fuel 308 and hydrolysate 310 via HTC 302 after which separation of liquid and solid is much easier. In the second stage 304, the biomass waste-derived hydrolysate 310 with high content of organic matter may be further reformed into H₂- and CH₄-rich fuel gas 312 using catalytic aqueous phase reforming (CAPR) under mild temperature and pressure.

[0053] The first stage 302 may be carried out in a first reactor, and the second stage 304 may be carried out in a second reactor. In various embodiments, the first stage 302 may be carried out in one or more further reactors in addition to the first reactor. Also, the second stage 304 may include one or more further reactors in addition to the second reactor.

[0054] In various embodiments, a two-stage system may be provided. The two-stage system may use two sequential processes. The system may include a first stage and a second stage. CAPR may follow HTC in a sequential manner. Initially, biomass feedstocks may be fed into the first reactor, i.e. the HTC reactor. Subsequently, the resulting slurry may be transferred to a separation unit to easily separate the hydrochar and hydrolysate products. In various embodiments, the first stage may include separating the slurry obtained from hydrothermal carbonization into the solid fuel (i.e. the hydrochar) and the hydrolysate. The hydrochar may be used as solid fuel of superior fuel quality, while the hydrolysate may be subsequently fed into the second reactor, i.e. the CAPR reactor. In the second stage 304, hydrogen- and methane-rich fuel gas may be generated from the hydrolysate.

[0055] Moreover, both HTC and CAPR may be implemented in continuous flow reactors in which biomass feedstocks are processed continuously by HTC to produce sufficient hydrolysate supply for CAPR. In other words, a continuous flow system may be provided. The first stage 302 may be configured to continuously provide the hydrolysate to the second stage 304, e.g. via pipes. The second stage 304 may be configured to continuously receive the hydrolysate. The second stage 304 may be configured to continuously generate the one or more fuel gases from the hydrolysate. The first reactor may be configured to continuously provide a slurry to the separation unit, e.g. via pipes. The separation unit may be configured to continuously receive the slurry, and further configured to separate the slurry into the solid fuel and the hydrolysate in a continuous manner. For instance, the separation unit may include a mechanical press or a chamber including a centrifuge for separating the slurry into the solid fuel and the hydrolysate. Using a mechanical press or centrifugation may advantageously be less energy-intensive than using evaporation by heating. The hydrolysate may be used in subsequent CAPR as feedstock. The separation unit may be further configured to continuously provide the hydrolysate to the second reactor, e.g. via pipes. The second reactor may be configured to continuously receive the hydrolysate. The second reactor may be configured to continuously generate the one or more fuel gases from the hydrolysate. In the continuous CAPR reactor, fuel gases may be continuously produced for downstream consumption. In this way, continuous processing of biomass and generation of fuels (i.e. hydrochar and fuel gases) may be realized simultaneously.

[0056] A 20 g cellulose feedstock with a moisture content of 85% was fed into a 50 mL Parr reactor for HTC under 200 °C and autogenously generated pressure (about 40 bars) for 6 hours. After HTC, solid and liquid products were readily separated and 58% hydrochar solid fuel was recovered from one kg dry cellulose. The gas product turned out to be CO₂. Subsequently, in the second stage, a 20 mL hydrolysate solution with high organic content from the first stage was fed into the same reactor together with 0.5 g Ru/C. Then the reactor was purged with N₂ gas for 5 min and an initial N₂ pressure of 30 bars was set at room temperature. The CAPR experiment was conducted at 220 °C and autogenously generated pressure (about 80 bars) for another 4 hours. Afterwards, the gas product was collected in a gas bag and analyzed using Agilent gas chromatography – thermal conductivity detector (GC TCD). The gas composition and yield are shown in FIG. 4.

[0057] FIG. 4 is a table 400 showing the gas composition and yield during catalytic aqueous phase reforming of hydrolysate derived from hydrothermal carbonization of cellulose according to various embodiments. 20 millilitres (mL) aqueous feedstock, 220 °C, 30 bar initial N₂ pressure, and 4 hours of residence time were used as experimental conditions.

[0058] In the final gas, H₂, CH₄ and CO₂ were the main gas components. Particularly, H₂ and CH₄ accounted for about 13% and 35% respectively, in the gas product composition. The yield of H₂ and CH₄ could be further optimized. Overall, 122.8 litres (L) H₂ and 324.8 litres (L) CH₄ may be generated from one kg organic matter in the hydrolysate from HTC of cellulose.

[0059] Overall, it may be feasible to effectively harness energy from wet biomass waste streams using the proposed two-stage hydrothermal conversion system. Each individual process (i.e. HTC and CAPR) in this two-stage system may have its advantage and weakness. However, the advantage of one process may be used to offset the weakness of the other. Specifically, HTC may not only improve the dewaterability of wet biomass waste but may also recover solid fuel of better fuel quality. Nonetheless, the amount of hydrochar obtained may be lower than raw biomass solid due to hydrolysis therein. On the other hand, when CAPR is applied for treatment of raw biomass waste, catalysts may be easily deactivated as a result of carbonization reaction. Therefore, HTC may be first used to facilitate hydrolysis, resulting in hydrolysate with small organic molecules. Hydrochar may be recovered from wet biomass waste after simple separation of liquid and solid phases. The homogeneous and organic matter-rich aqueous solution may then be fed into CAPR process to catalytically decompose organic molecules in solution into H₂- and CH₄-rich fuel gas without severe catalyst deactivation. Thus, various embodiments may simultaneously treat wet biomass waste with higher solid content (i.e. significant waste reduction) and extract fuel products from raw waste to a great extent. The wet biomass waste-derived hydrochar solid fuel may be used as an alternative coal fuel in co-firing power plant whereas the H₂ and CH₄ may be used as fuel gas. From the perspective of commercial applications, various embodiments may be applied to significantly recover cleaner solid fuel and H₂/CH₄ fuel gas from wet biomass waste streams with the avoidance of pre-drying step and severe catalyst deactivation compared with conventional technologies or reactor systems.

[0060] In addition, the operating conditions may be optimized based on evaluation of cost and product quality in commercial plants.

[0061] In the first HTC process, the temperature range may be from 180 to 250 °C, pressure range may be from 20 to 100 bars, and reaction time may be from 1 to 24 hours. In the second CAPR process, temperature range may be from 200 to 350 °C, pressure range may be from 30 to 150 bars, and reaction time may be from 1 to 12 hours. Due to the elimination of catalyst clogging, a continuous process design may also be used for CAPR.

[0062] The wet biomass waste streams may be food waste, sewage sludge, algae, animal manures (e.g. chicken and swine manures, cattle dung), human waste, horticulture waste, and so-called biomass wastes. The wet biomass waste streams may also include fruit peels, bagasse, winery waste or distilled grains, corn stalk, rice husk, and aquatic, terrestrial or even arid land plants, etc.

[0063] The solid content of the wet biomass waste streams for HTC treatment may be quite flexible, ranging from about 5 wt.% to about 50 wt.%.

[0064] The catalyst may consist of two components, i.e. the metal and the supporting material. Effective metal catalysts that may be used in CAPR may include noble metals supported on carbon materials. The noble metals may be Ru, Pt, Pd, and/or a combination of these noble metals. The carbon supporting materials may be activated carbon, carbon nanotubes (i.e. multi-walled carbon nanotubes and single-walled carbon nanotubes) and graphene. The support materials may also be extended to Al₂O₃, TiO₂, ZrO₂, and CeO₂. In addition, other bases and transition metals may be used as promoters in the metal catalysts to facilitate H₂ and CH₄ gas production. The main promoters may include Ni, Co, Rh, Cu, Fe, Mg, K, Ca, Na, and Cs.

[0065] Alkali additives may be used to enhance the yield and purity of H₂ in the final fuel gas. Additives may include CaO, NaOH, KOH, NaHCO₃, and KHCO₃. Other alkali additives, such as Ca(OH)₂, Na₂CO₃, K₂CO₃, mixtures of the alkali additives, and natural materials containing any of these effective additives (e.g. Trona), may also be effective to promote the yield and purity of H₂ in the final fuel gas.

[0066] **Example 2**

[0067] FIG. 5 is an image 500 showing a reactor used for hydrothermal carbonization (HTC) according to various embodiments. The reactor may be a high temperature and pressure (high T and P) Parr reactor.

[0068] FIG. 6 is a graph 600 showing the moisture content and ash content for raw sewage sludge and hydrochars after hydrothermal carbonization under different residence time according to various embodiments. The graph 600 shows that dewatered sewage sludge (DSS) has a moisture content of about 84.0% and an ash content of about 37.1%. Hydrochar-4, which is obtained after 4 hours of HTC, has a moisture content of about 75.7% and an ash content of about 53.3%. Hydrochar-6, which is obtained after 6 hours of HTC, has a moisture content of about 63.3% and an ash content of about 54.8%. As observed from FIG. 6, moisture content may decrease, and relative ash content may increase with increasing durations of hydrothermal carbonization.

[0069] FIG. 7A is an image 700a showing containers with ash residue from raw sewage sludge (702a), ash residue from hydrochar obtained after 4 hours of hydrothermal carbonization (704a), and ash residue from hydrochar obtained after 6 hours of hydrothermal carbonization (706a) according to various embodiments. FIG. 7B is an image 700b showing ash residue from raw sewage sludge (702b), ash residue from hydrochar obtained after 4 hours of hydrothermal carbonization (704b), and ash residue from hydrochar obtained after 6 hours of hydrothermal carbonization (706b) according to various embodiments.

[0070] FIG. 8 is an image 800 of pellets of raw sewage sludge (802), pellets of hydrochar obtained after 4 hours of hydrothermal carbonization (804), and pellets of hydrochar obtained after 6 hours of hydrothermal carbonization (806) according to various embodiments.

[0071] FIG. 9 is a plot 900 of higher heating value (megajoule per kilogram or MJ/kg) of raw sewage sludge, hydrochar obtained after 4 hours of hydrothermal carbonization, and hydrochar obtained after 6 hours of hydrothermal carbonization according to various embodiments on dry basis (DB) and on dry- and ash-free basis (DAF). DAF samples generally show an increased higher heating value (HHV) compared to DB samples. The higher heating value (HHV) may also be referred to as a gross calorific value (GCV). The higher heating values of the DB samples decrease with increasing durations of HTC, while the higher heating values of the DAF samples increase with increasing durations of HTC.

[0072] FIG. 10 is a plot 1000 of solid hydrochar yield (percent or %) after hydrothermal carbonization under different residence time (i.e. 4 hours and 6 hours), and the chemical oxygen demand (COD) (gram per liter or g/L) for the corresponding aqueous phases according to various embodiments. The percentage yield of solid hydrochar after 4 hours of HTC may be about 63.2%, while the percentage yield of solid hydrochar after 6 hours of

HTC may be about 47.3%. The COD of the aqueous phase obtained after 4 hours of HTC may be about 69.4 g/mL, while the COD of the aqueous phase obtained after 6 hours of HTC may be about 72.5 g/mL.

[0073] FIG. 11 is an image 1100 of the aqueous phases obtained after 4 hours of hydrothermal carbonization (1102) and after 6 hours of hydrothermal carbonization (1104) according to various embodiments.

[0074] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method for converting biomass to fuel products, the method comprising:

generating a solid fuel and a hydrolysate from said biomass via a hydrothermal carbonization process; and

generating one or more fuel gases from the hydrolysate via a catalytic aqueous phase reforming process.
2. The method according to claim 1,

wherein the hydrothermal carbonization process is carried at a temperature selected from a range of about 180 °C to about 250 °C.
3. The method according to claim 1 or claim 2,

wherein the hydrothermal carbonization process is carried out at a pressure selected from a range of about 20 bars to about 100 bars.
4. The method according to any one of claims 1 to 3,

wherein the hydrothermal carbonization process is carried out for a duration selected from about 1 hour to about 24 hours.
5. The method according to any one of claims 1 to 4,

wherein the catalytic aqueous phase reforming process is carried out at a temperature selected from a range of about 200 °C to about 350 °C.

6. The method according to any one of claims 1 to 5,

wherein the catalytic aqueous phase reforming process is carried out at a pressure selected from a range of about 30 bars to about 150 bars.

7. The method according to any of claims 1 to 6,

wherein the catalytic aqueous phase reforming process is carried out for a duration selected from about 1 hour to about 12 hours.

8. The method according to any one of claims 1 to 7,

wherein the catalytic aqueous phase reforming process is carried out in the presence of a catalyst.

9. The method according to claim 8,

wherein the catalyst is a metal catalyst.

10. The method according to claim 9,

wherein the metal catalyst is selected from a group consisting of ruthenium, platinum, palladium, and any combination thereof.

11. The method according to any one of claims 8 to 10,

wherein the catalyst is on a suitable support comprising a suitable material selected from a group consisting of carbon, aluminium oxide, titanium oxide, zirconium oxide, and cerium oxide.
12. The method according to any one of claims 8 to 11,

wherein the catalytic aqueous phase reforming process is carried out in the presence of the catalyst with a suitable promotor selected from a group consisting of nickel, cobalt, rhodium, copper, iron, magnesium, potassium, calcium, sodium, and caesium.
13. The method according to any one of claims 8 to 12,

wherein the catalytic aqueous phase reforming process is carried out in the presence of the catalyst with a suitable additive selected from a group consisting of calcium oxide, calcium hydroxide, sodium hydroxide, potassium hydroxide, sodium bicarbonate, potassium bicarbonate, sodium carbonate, potassium carbonate, and any mixtures thereof.
14. The method according to any one of claims 1 to 13,

wherein the biomass has a solid content selected from a range of about 5 weight percent to about 50 weight percent.
15. The method according to any one of claims 1 to 14,

wherein the biomass is selected from a group consisting of food waste, sewage sludge, algae, animal manure, human waste, horticulture waste, fruit peels, bagasse, winery waste, distilled grains, corn stalks, rice husks, aquatic plants, terrestrial plants, arid land plants, and any combination thereof.

16. The method according to any one of claims 1 to 15,

wherein the one or more fuel gases comprise hydrogen gas.
17. The method according to any one of claims 1 to 16,

wherein the one or more fuel gases comprise methane.
18. A system for converting biomass to fuel products, the system comprising:

a first stage configured to generate a solid fuel and hydrolysate from said biomass; and

a second stage configured to generate one or more fuel gases from the hydrolysate.
19. The system according to claim 18,

wherein the first stage is in a first reactor and the second stage is in a second reactor.
20. The system according to claim 18 or claim 19,

wherein the biomass has a solid content selected from a range of about 5 weight percent to about 50 weight percent.

21. The system according to any one of claims 18 to 20,

wherein the one or more fuel gases comprise hydrogen gas.

22. The system according to any one of claims 18 to 21,

wherein the one or more fuel gases comprise methane.

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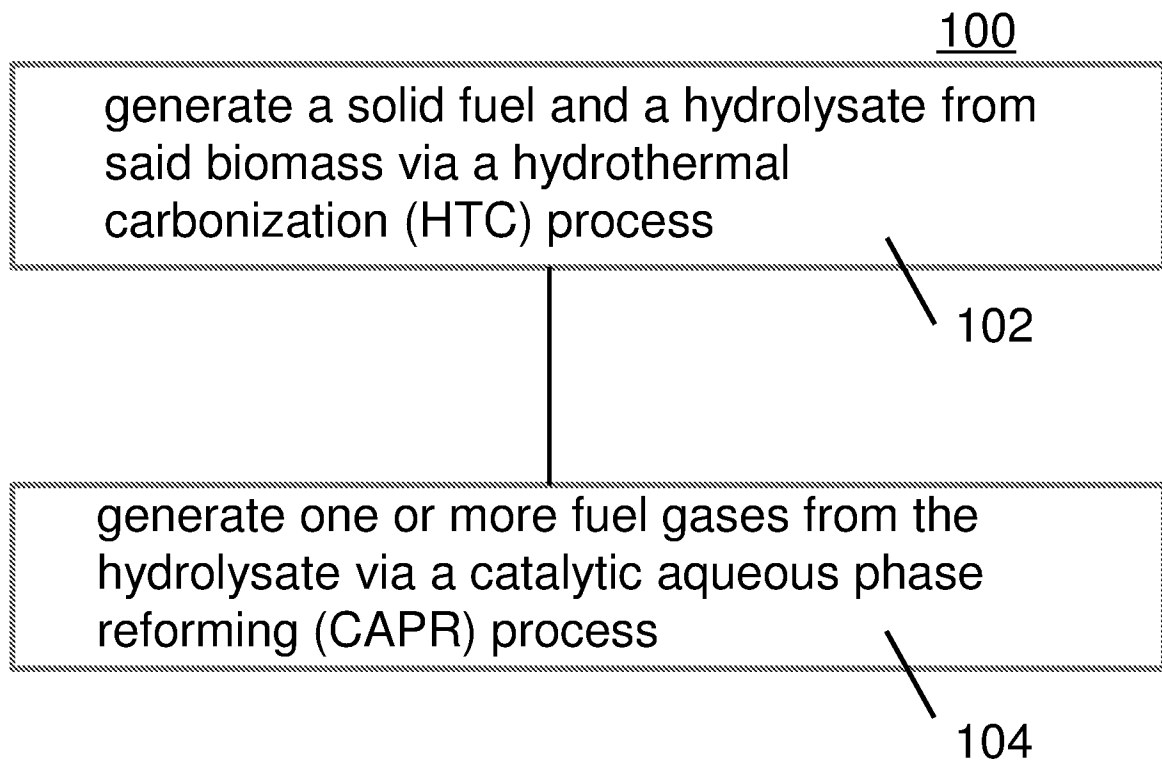
FIG. 1

FIG. 2

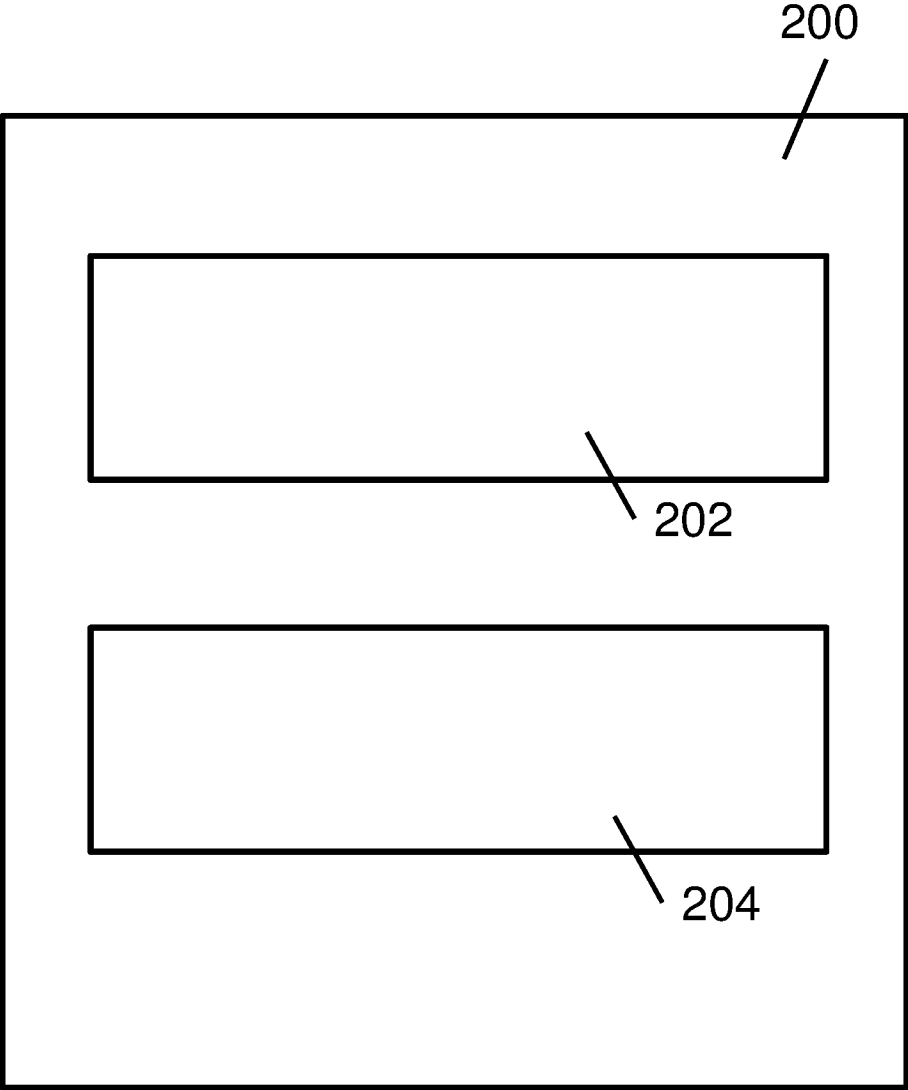
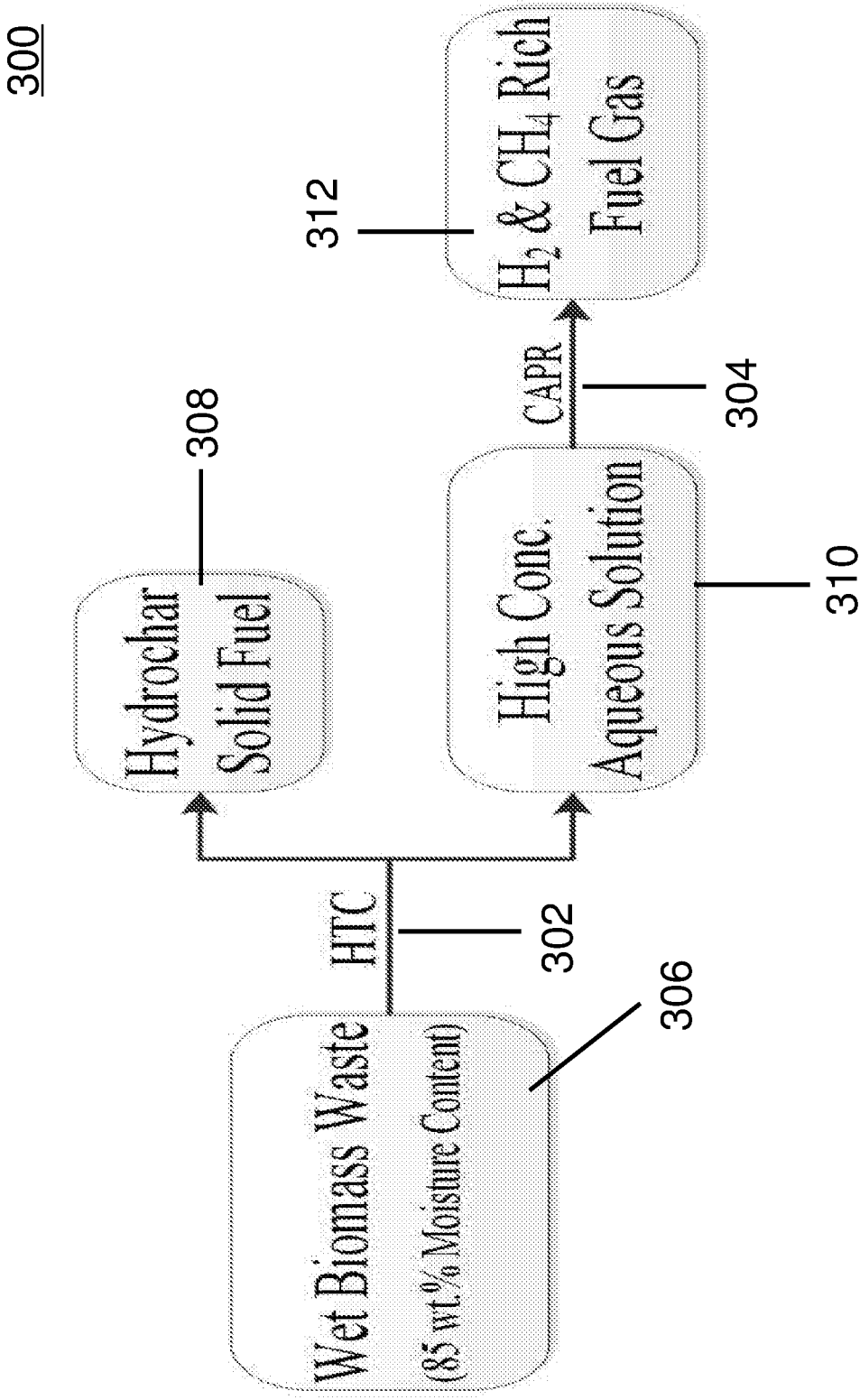


FIG. 3



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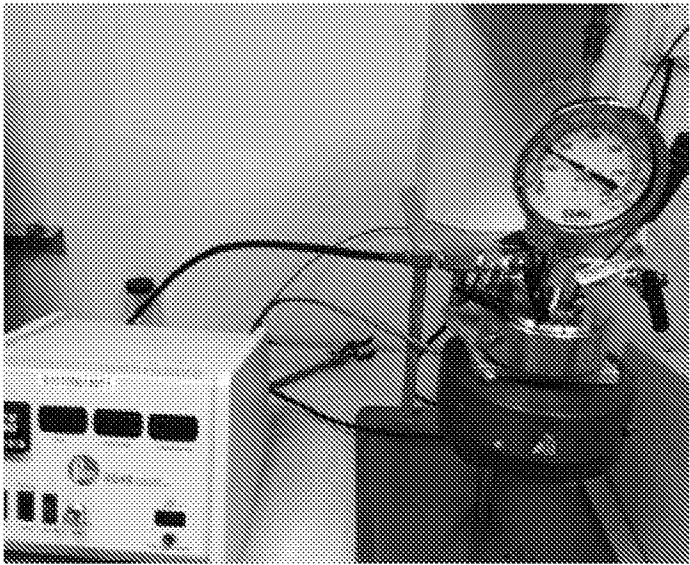
FIG. 4

400

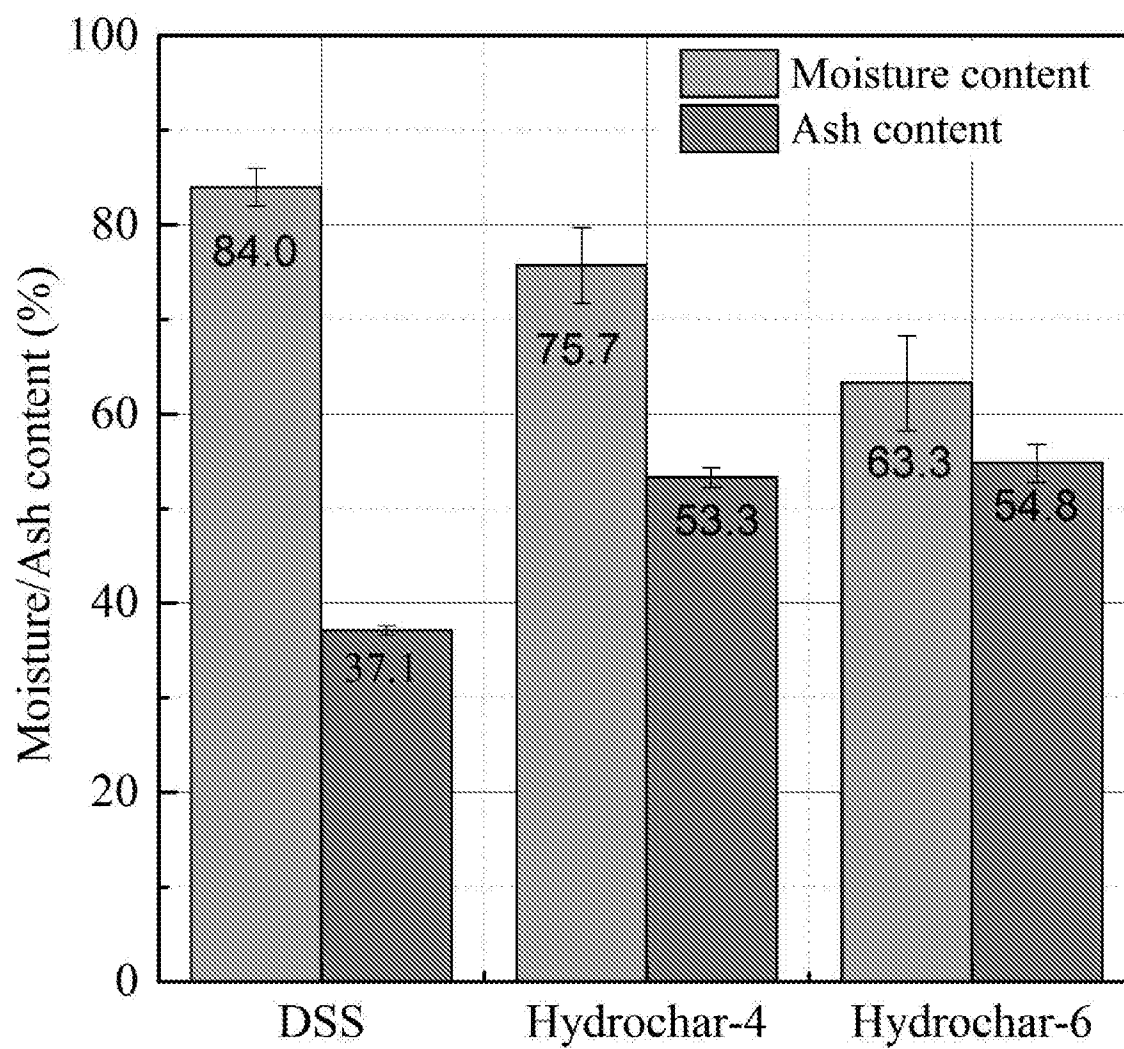
Main gas	Gas composition (vol.%)	Gas yield (L/kg organic matter in hydrolysate from HTC)
H ₂	13.1	122.8
CH ₄	34.6	324.8
CO ₂	52.3	490.4

FIG. 5

500



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FIG. 6600

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FIG. 7A

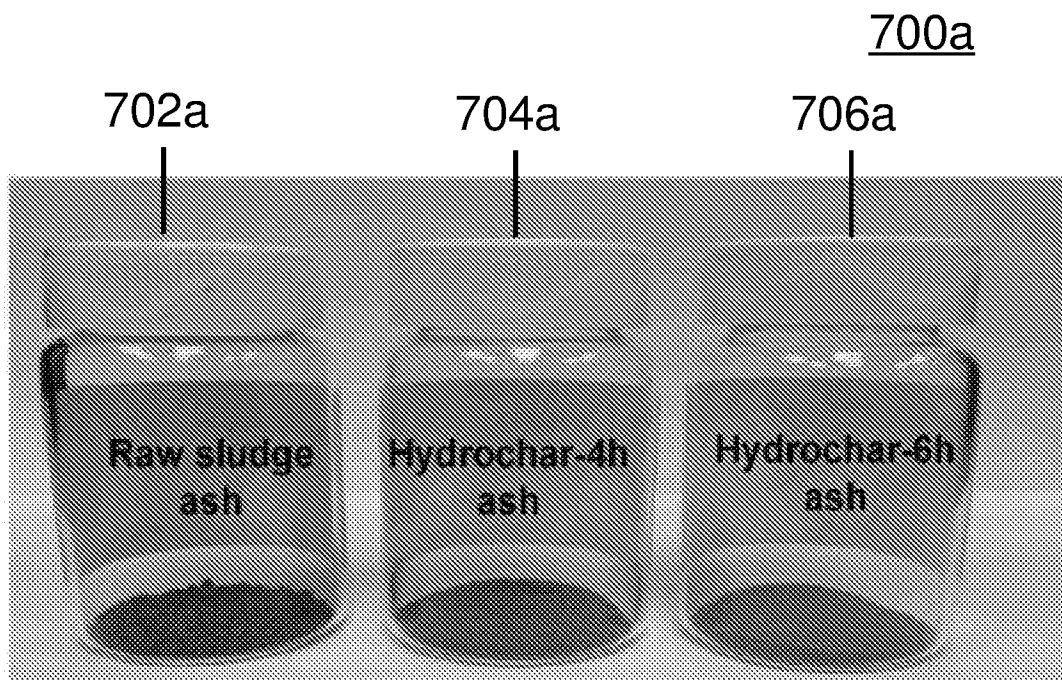


FIG. 7B

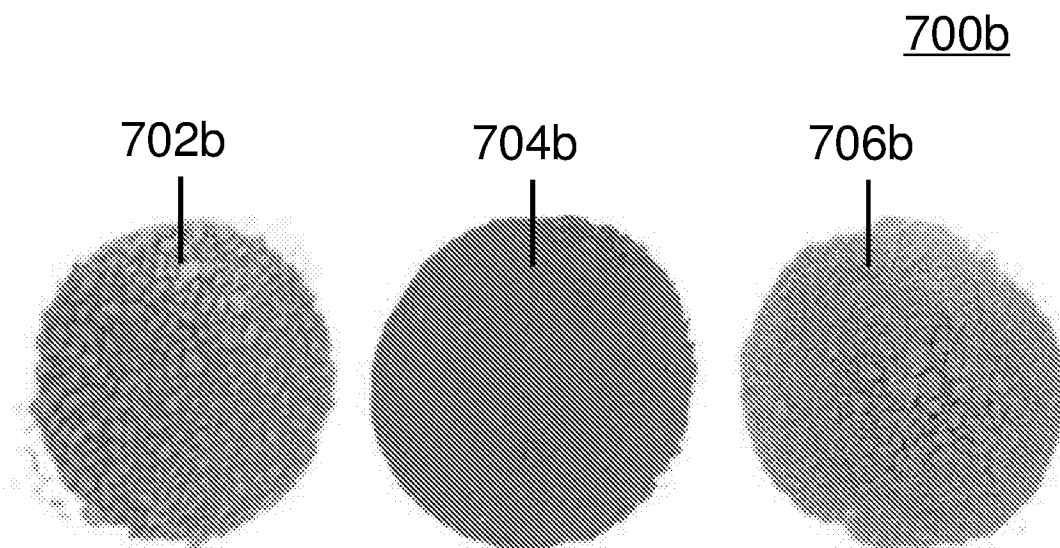


FIG. 8

800

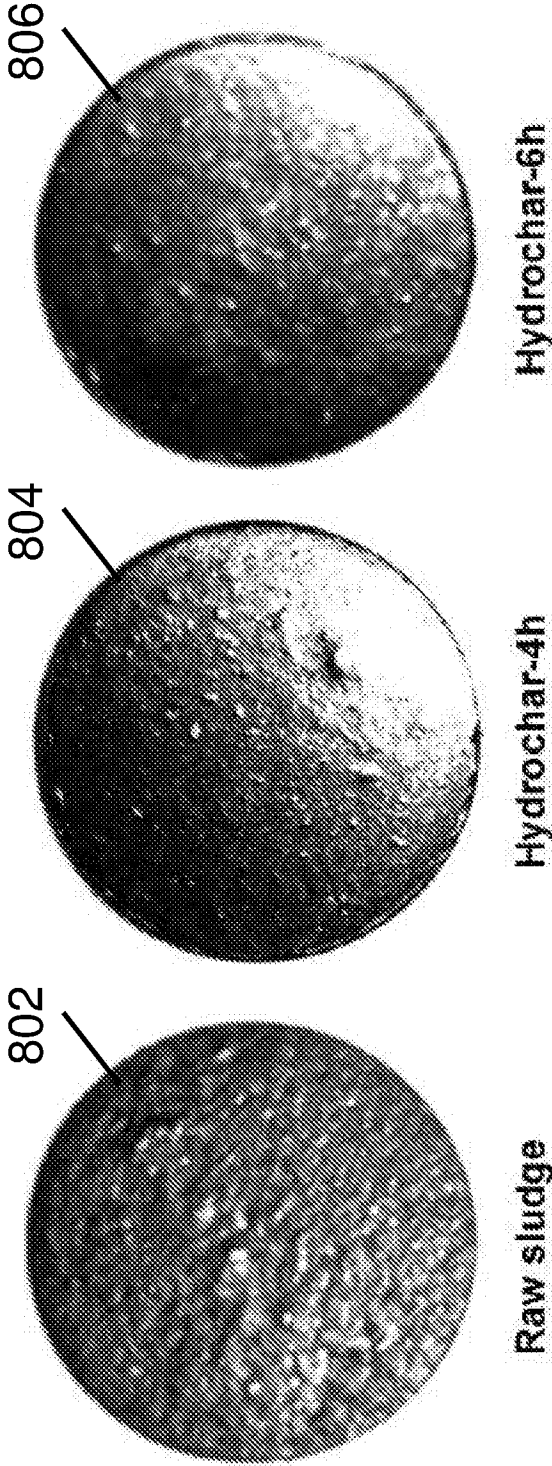
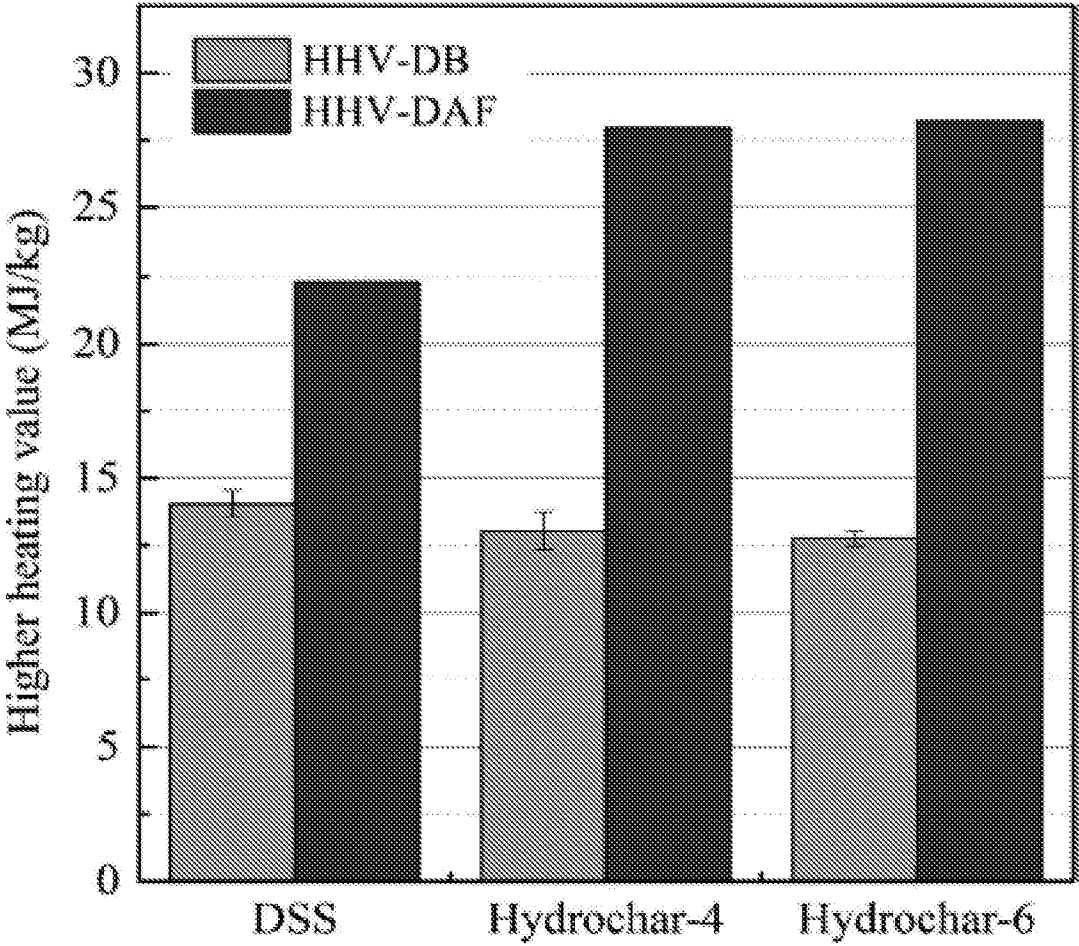


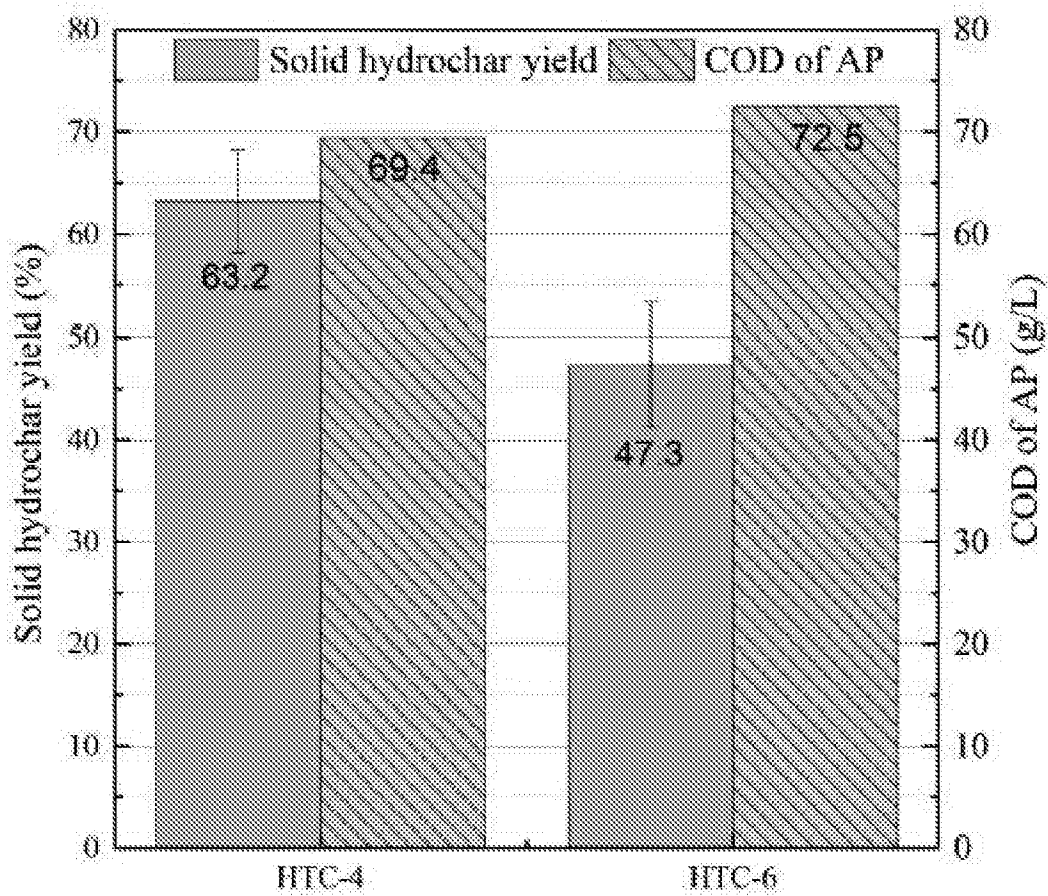
FIG. 9

900



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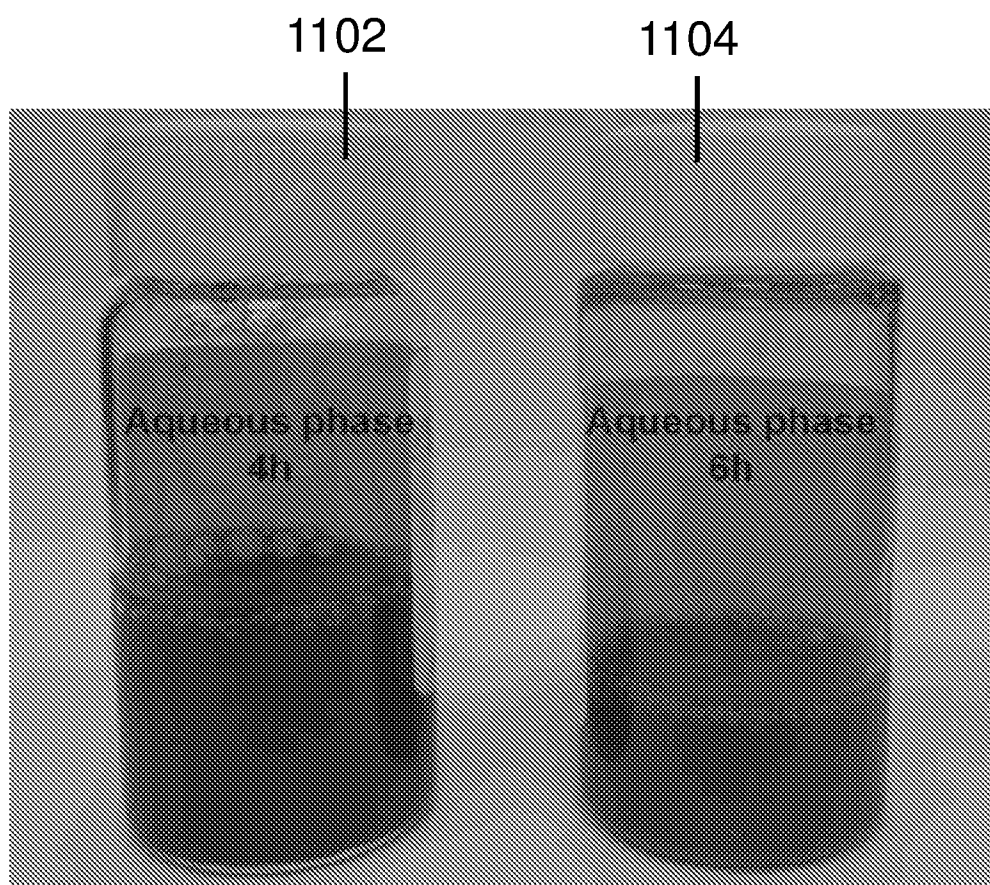
FIG. 10

1000

10/10

FIG. 11

1100



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050259

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B09B, C02F, C10B, C10L

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)

Databases: Registry, CAPLUS, FAMPAT

Keywords: biomass, sludge, hydrothermal conversion, hydrothermal carboni[z,s]ation, HTC, aqueous phase reforming, APR, CAPR, fuel gas, bio gas, methane, hydrogen, 水热, 生物质, 生物废料, , 有机废料, 污泥, and related search terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2014/0275299 A1 (BEDWELL W. B. ET AL.) 18 September 2014 para [0008-0009, 0011, 0016, 0019, 0021-0027, 0029]; claims 1-4, 8-10	18-22 1-17
X	US 2012/0073199 A1 (LEWIS F. M) 29 March 2012 Abstract; para [0026-0027, 0029-0031, 0035, 0046-0051, 0055, 0057-0058, 0066, 0074, 0077-0078, 0081, 0083]; claims 1-5; Figures 1-4	18-19, 22
X	US 2004/0182779 A1 (KILIAN R. E. ET AL.) 23 September 2004 Abstract; para [0001, 0007, 0012, 0015]; claim 1; Figure 1	18-19, 22

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"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

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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

"&" document member of the same patent family

Date of the actual completion of the international search

20/07/2016

(day/month/year)

Date of mailing of the international search report

23/08/2016

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050259

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8658414 B2 (HORNUNG A. ET AL.) 25 February 2014 col 1 lines 15-17, col 2 lines 7-16, col 4 line 26-67, col 5 lines 9-17; claims 1, 4	18-19, 21
A	WO 2012/177138 A1 (UNIVERSITEIT UTRECHT HOLDING B. V.) 27 December 2012 Abstract; page 1 lines 5-9, page 4 lines 1-17, page 5 line 28 - page 6 line 12, page 7 line 3 – page 8 line 7	
A	ALONSO D. M. ET AL., Catalytic conversion of biomass to biofuels. <i>Green Chemistry</i> , 6 August 2010, Vol. 12, pages 1493-1513 [Retrieved on 2016-07-20] <DOI: DOI: 10.1039/C004654J> Abstract; Sections 2-4, 5.2, 5.4, 6, 8, 9-10	
A	LIBRA J. A. ET AL., Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. <i>Biofuels</i> , 9 April 2014, Vol. 2, pages 89-124 [Retrieved on 2016-07-20] <DOI: 10.4155/bfs.10.81> Abstract; pages 89-90, page 92 Hydrothermal processes, Table 1, page 94 Reactions, page 95 Products	
A	HE C. ET AL., Hydrothermal gasification of sewage sludge and model compounds for renewable hydrogen production: A review. <i>Renewable and Sustainable Energy Reviews</i> , 31 August 2014, Vol. 39, pages 1127-1142 [Retrieved on 2016-07-12] <DOI: 10.1016/J.RSER.2014.07.141> Abstract; Sections 1, 2, 2.1, 3; Table 3	
P,X	WO 2016/023563 A1 (INBICON A/S) 18 February 2016 page 5 lines 6-16, page 7 lines 20-31, page 39 lines 7-page 40 line 28, page 41 lines 16-26, page 43 lines 19-29	18-19, 22
P,X	CN 105331376 A (UNIV HUAZHONG AGRICULTURAL) 17 February 2016 Abstract; para [0007]; Examples	18-20, 22

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050259

Supplemental Box

(Classification of Subject Matter)

Int. Cl.

C02F 11/10 (2006.01)

C10B 53/02 (2006.01)

C10L 3/08 (2006.01)

C10L 5/40 (2006.01)

C10L 5/42 (2006.01)

C10L 5/44 (2006.01)

C10L 5/46 (2006.01)

C02F 9/00 (2006.01)

C02F 9/02 (2006.01)

C02F 9/08 (2006.01)

C10L 9/08 (2006.01)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2016/050259

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

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