(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 May 2010 (20.05.2010)

PCT

(10) International Publication Number
WO 2010/056463 A2

(51) **International Patent Classification**:
C12P 3/00 (2006.01) ***C02F 3/00*** (2006.01)
C12M 1/107 (2006.01)

(21) **International Application Number**:
PCT/US2009/060813

(22) **International Filing Date**:
15 October 2009 (15.10.2009)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
61/113,848 12 November 2008 (12.11.2008) US

(71) **Applicant** *(for all designated States except US)*: **UNI-CONTROL, LLC** [US/US]; Dupont Brandy Wine Building, 1000 N. West St., Suite 1200, Wilmington, Delaware 19801 (US).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **JENSEN, Jens Wiik** [DK/DK]; Ahlmanns Alle 19, DK-2900 Hellerup (DK). **DICKMAN, Eric** [US/US]; 5 Morseland Ave., Newton, Massachusetts 02459 (US).

(74) **Agents**: **WESTBY, Timothy S.** et al.; CONLEY ROSE, P.C., P. O. Box 3267, Houston, Texas 77253-3267 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) **Title**: WASTE TO ENERGY PROCESS COMPRISING BIOLOGICAL WATER SHIFT REACTION USING CARBON MONOXIDE PRODUCED VIA GASIFICATION TO PRODUCE HYDROGEN

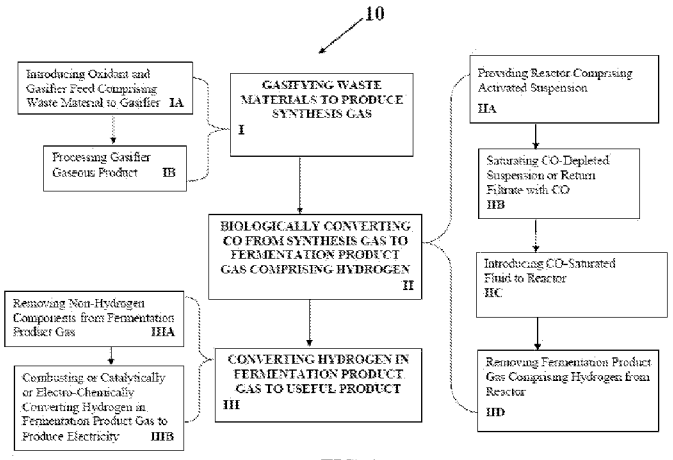

FIG. 1

(57) **Abstract**: A waste to energy method comprising: gasifying a feed material comprising waste, to produce gasifier gaseous product comprising synthesis gas and a gasifier non-gaseous product; biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen, wherein at least a portion of the carbon monoxide is obtained from the gasifier gaseous product; and utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel. Biologically converting may comprise introducing a fermentation feed gas into a deep shaft reactor, wherein the deep shaft reactor contains a suspension comprising a liquid nutrient medium lacking a carbon source and photoactivated microorganisms capable of carrying out the water-gas shift reaction; has a vertical depth and a shaft width; comprises a downcomer and a riser separated by a divider; and comprises a headspace above a normal operating suspension fill line.

WO 2010/056463 A2

WASTE TO ENERGY PROCESS COMPRISING BIOLOGICAL WATER SHIFT REACTION USING CARBON MONOXIDE PRODUCED VIA GASIFICATION TO PRODUCE HYDROGEN

FIELD OF THE INVENTION

[0001] This invention relates generally to microbial production of hydrogen gas by biological water shift reaction using a CO-containing feed gas derived from plasma gasification of opportunity fuels.

BACKGROUND

[0002] Carbon-based wastes represent one of the most promising yet substantially untapped renewable energy sources. Over a billion tons of municipal solid waste (MSW), agricultural, forestry, bio-solids, and other waste products are generated annually in the United States alone.

[0003] Disposing waste biomass via gasification provides certain benefits when compared with land application, landfilling and incineration. For example, via gasification, only the inorganic fraction of the waste feed, i.e., the glass, ash, metal, is not converted into gaseous product gas comprising synthesis gas. Thus, the lives of landfills may be extended by gasification of waste to produce valuable synthesis gas.

[0004] Additionally, substantial tax credits may be available for waste-to-electricity generation, making such processes economically desirable. Furthermore, the slag produced via gasification may be environmentally friendly, and the gasification may produce reduced or negligible amounts of water and air emissions.

[0005] Tons of biosolids are annually disposed of in the United States via spreading on agricultural land. Resistance to such practice is increasing in light of potential adverse health affects to humans. Waste to energy processes will help reduce or eliminate such spreading practices.

[0006] Utilization of conventionally non-valuable wastes, such as corn stalks and cotton plants may provide additional income for farmer's from existing crops.

[0007] Hydrogen (H_2) is an attractive alternative to fossil fuels as a portable, non-polluting source of energy. Today, hydrogen gas is predominantly produced by reforming fossil sources (petroleum, natural gas and coal) to produce synthesis gas (syngas), which is a mixture of hydrogen and carbon monoxide (CO). Syngas is customarily generated by steam or dry reforming or partial oxidation of natural gas or liquid hydrocarbons, by gasification of

coal, or by waste-to-energy gasification processes (*e.g.*, biomass gasification). The relative amounts of CO and H_2 in a syngas product varies depending upon the way it is generated. Existing technologies for separating and purifying the hydrogen component of syngas usually involve pressure swing adsorption (PSA), membrane separation, or chemical reaction on solid iron oxide and calcium oxide beds, with regeneration of the solids.

[0008] Different technologies such as electrolysis and thermolysis have been investigated for producing hydrogen from water. Still other technologies used for hydrogen production include inorganic chemical reduction and various biological reactions. The biological production of hydrogen using photosynthetic and fermentative microorganisms has been described. Among these microorganisms are certain photosynthetic bacteria that contain a carbon monoxide oxidation pathway in which the water-gas shift reaction occurs, converting a mole of water and a mole of carbon monoxide into equimolar amounts of hydrogen and carbon dioxide. The water-gas shift reaction has been reported for *Rubrivivax gelatinosus*, *Rhodospirillum rubrum, Rhodopseudomonas palustris*, and others.

[0009] As the CO substrate is of low solubility in an aqueous solution, mass transfer of CO into the microbial culture medium is likely the rate-limiting step for the biological water-gas shift reaction. A challenge in developing synthesis gas fermentation processes is providing for efficient gas mass transfer, and resolving microbial toxicity issues with respect to CO and CO_2 gases.

[0010] Hydrogen may be used as fuel for the production of electricity via combustion with additional fuel in a gas generator set, or other combustion unit. High-purity hydrogen may be used as fuel in fuel cells for the production of electricity.

[0011] There exists a need for a method of converting waste to energy via gasification of waste materials to produce synthesis gas (and additionally to gasify coal, wood chips, bitumen, biomass and sludge in a more environmentally friendly manner), microbial fermentation-polishing of the gasification-produced synthesis gas to produce high-purity hydrogen in bulk, and production of electricity via the biologically-produced hydrogen. Desirably, the method produces minimal amounts of environmentally-undesirable (leaching) slag, air emissions, and water emissions.

SUMMARY

[0012] In accordance with certain embodiments of the invention, herein disclosed is a waste to energy method comprising: gasifying a feed material comprising waste, to produce gasifier gaseous product comprising synthesis gas and a gasifier non-gaseous product, wherein gasifying is performed at a gasification temperature and a gasification pressure;

biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen, wherein at least a portion of the carbon monoxide is obtained from the gasifier gaseous product; and utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel. Biologically converting may comprise introducing a fermentation feed gas into a deep shaft reactor, wherein the deep shaft reactor contains a suspension comprising a liquid nutrient medium lacking a carbon source and photoactivated microorganisms capable of carrying out the water-gas shift reaction; has a vertical depth and a shaft width; comprises a downcomer and a riser separated by a divider; and comprises a headspace above a normal operating suspension fill line. Microorganisms capable of carrying out the water-gas shift reaction may be selected from the group consisting of *Rubrivivax gelatinosus*, *Rhodospirillum rubrum,* and *Rhodopseudomonas palustris*.

[0013] In embodiments of the method, biologically converting further comprises: saturating a fluid with CO gas by contacting, under pressure, the fluid with fermentation feed gas comprising CO in a retention chamber; introducing the saturated fluid into the riser of the deep shaft reactor such that the suspension within the deep shaft reactor circulates about the divider flowing with a first linear velocity up the riser, passing over the top of the divider, and flowing with a second linear velocity down the downcomer, wherein the first linear velocity is greater than the second linear velocity; and vacuum degasifying a product gas comprising hydrogen from the headspace, whereby suspension circulating from the top of the divider down into the downcomer becomes CO-depleted. The method may further comprise maintaining a desired level of total dissolved solids within the deep shaft reactor by continuously, periodically or semi-continuously removing an extracted portion of suspension from a top portion of the deep shaft reactor. Microorganisms may be separated from the extracted portion of suspension to produce a sludge comprising separated microorganisms and a biomass-reduced effluent. Microorganisms may be separated from the extracted portion of suspension via ultrafiltration, microfiltration, centrifugation, decanting, clarification, or a combination thereof. At least a portion of the biomass-reduced effluent may be recycled to the deep shaft reactor. The fluid saturated with CO may comprise at least a portion of the biomass-reduced effluent.

[0014] In embodiments, the method further comprises gasifying at least a portion of the sludge to produce additional gasifier gaseous product comprising synthesis gas. In embodiments, at least a portion of the extracted suspension is utilized to produce methane gas via fermentation. At least a portion of the biomass in the extracted suspension may be

combined with suitable substrates and fermented to produce at least one selected from butanol, ethanol and acetone.

[0015] In applications, the method further comprises extracting a CO-depleted portion of suspension from a lower portion of the downcomer, and the fluid comprises at least a portion of the CO-depleted portion of suspension extracted from the lower portion of the downcomer.

[0016] The method may further comprise adjusting the pH of the suspension to a pH of greater than about pH 9, such that carbon dioxide is converted to soluble bicarbonate. In embodiments, the majority of the biological conversion is performed in the absence of substantial light. Introducing CO-saturated fluid into the riser of the deep shaft reactor may comprise injecting CO-saturated fluid to at least one location within the riser via at least one high pressure pump and at least one injection nozzle or sprayer. Introducing CO-saturated fluid into the riser of the deep shaft reactor may comprise injecting CO-saturated fluid to a plurality of locations within the riser via a plurality of high pressure pumps and a plurality of injection nozzles or sprayers.

[0017] In embodiments of the method, there is no direct introduction of feed source into the downcomer of the deep shaft reactor. The method may further comprise forming a mixture comprising the fluid and the fermentation feed gas and increasing the pressure of the mixture.

[0018] The method may further comprise measuring the concentration of CO in the fermentation product gas comprising hydrogen and adjusting the volume of fermentation feed gas introduced into the deep shaft reactor, the concentration of carbon monoxide in the fermentation feed gas introduced into the deep shaft reactor, the level of TDS (total dissolved solids) in the deep shaft reactor, or a combination thereof such that the concentration of CO in the fermentation product gas is maintained below a desired value. Adjusting the concentration of CO in the fermentation feed gas may comprise combining at least a portion of the fermentation product gas with the fermentation feed gas as diluent. The desired value may be substantially zero.

[0019] The deep shaft reactor may have a vertical depth in the range of from about 50m to about 600m. The gasification temperature may be greater than about 2200°C. The gasification pressure may be about atmospheric pressure. Gasifying may comprise plasma gasifying. Plasma gasifying may further comprise introducing oxidant and feed material comprising waste into at least one plasma gasifier. The oxidant may be selected from oxygen-enriched air and oxygen.

[0020] In applications, the non-gaseous product passes EPA-mandated Toxicity Characteristic Leachate Procedure. The feed material comprising waste may be selected

from agricultural waste, forestry waste, biomass, municipal solid waste, auto shredder residue, yard waste, industrial waste, coal, bitumen, coke, and combinations thereof.

[0021] Biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen may be performed substantially anaerobically. Utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel may further comprise increasing the purity of the hydrogen in the fermentation product gas. Utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel may further comprise at least one selected from the group consisting of increasing the purity of the hydrogen in the fermentation feed gas via one or more hydrogen pressure swing adsorption units, combusting at least a portion of the fermentation product gas, and electrochemically converting at least a portion of the hydrogen to electricity.

[0022] The method may further comprise extracting heat from the gasifier gaseous product comprising synthesis gas. Extracting heat from the gasifier gaseous product may further comprise using the extracted heat for preheating oxidant, generating steam, or both. Particulate matter may be removed from the gasifier gaseous product.

[0023] These and other embodiments of the present invention, and various features and potential advantages will be apparent with reference to the following description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Figure 1 is a process flow diagram of an embodiment of a waste to energy method 10 comprising biologically converting carbon monoxide produced via gasification to fermentation product gas comprising hydrogen.

[0025] Figure 2 is a schematic illustration of a waste to energy (WTE) system 10a suitable for carrying out the disclosed method according to an embodiment of the invention.

[0026] Figure 3 is a schematic illustration of an upstream gasification zone 100a suitable for carrying out portions of the disclosed method according to embodiments of the invention.

[0027] Figure 4 is a schematic illustration of a downstream gasification zone 100b suitable for carrying out portions of the disclosed method according to embodiments of the invention.

[0028] Figure 5 is a schematic illustration of a WTE system 10b suitable for carrying out the disclosed method according to an embodiment of the invention; Figure 5 details a suitable deep-shaft reactor 30 for biologically converting CO to fermentation product gas comprising hydrogen and possible relation of the deep shaft reactor to hydrogen recovery system 110, biomass separation unit 90, retention chamber 80, and plasma gasification subsystem 100.

[0029] Figure 6 is a schematic illustration of a WTE system 10c suitable for carrying out the disclosed method according to another embodiment of the invention.

[0030] Figures 7b and 7b are horizontal cross sections of respective embodiments of a deep shaft reactor 30 suitable for carrying out portions of the disclosed method. Figure 7a shows an embodiment with one slow-flow zone and one fast-flow zone. Figure 7b shows an embodiment with one slow-flow zone and two fast-flow zones.

[0031] Figure 8a is a schematic of an embodiment of a hydrogen recovery subsystem 110a suitable for carrying out portions of the disclosed method.

[0032] Figure 8b is a schematic of another embodiment of a hydrogen recovery subsystem 110b suitable for carrying out portions of the disclosed method.

NOTATION AND NOMENCLATURE

[0033] For the purposes of this disclosure, the term "coupled to" includes direct and indirect fluid communication (*i.e.*, flow of gas, liquid or both) between the coupled components.

[0034] The terms “suspension” and “mixed liquor” are used herein to refer to a mixture of liquids, gas, and solids in a fermentation mixture.

[0035] For the purposes of this disclosure, the terms "CO fermentation" and "fermentation of carbon monoxide" refer to the production of energy by microorganisms via metabolic pathway(s) that include a net water-gas shift reaction whereby hydrogen and carbon dioxide products are produced using carbon monoxide as the carbon-containing food source.

DETAILED DESCRIPTION

Overview

[0036] Figure 1 is a process flow diagram of a method 10 of converting waste to energy disclosed herein. As depicted schematically in Figure 1, WTE method 10 comprises: (I) gasifying a feed material comprising waste (and/or wood, coal, biomass, bitumen, and etc.) to produce gasifier gaseous product comprising synthesis gas; (II) biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen, wherein at least a portion of the carbon monoxide is obtained from the gasifier gaseous product; and (III) converting at least a portion of the hydrogen in the fermentation product gas to useful product. Each of (I) to (III) will be described in the following description of the disclosed method.

[0037] Figure 2 is a schematic illustration of a waste to energy (hereinafter WTE) system 10a suitable for carrying out the disclosed method according to an embodiment of the invention. WTE system 10a comprises deep shaft reactor 30, retention chamber 80, biomass extraction unit 90, hydrogen recovery subsystem 110, and plasma gasification subsystem 100, each of which will be described in detail hereinbelow.

[0038] Within WTE system 10a, deep-shaft reactor 30 is fluidly connected with hydrogen recovery subsystem 110, via outlet line 88, which connects a headspace 44 of deep-shaft reactor 30 with hydrogen recovery subsection 110. Deep-shaft reactor 30 is also fluidly connected with biomass extraction unit 90 via spent biomass outlet line 89, which connects a position of deep-shaft reactor 30 below operational fill line 43 with biomass extraction unit 90 which may operate via centrifugation. An outlet line 92 of biomass extraction unit 90 may be connected via a line 93 to an inlet 41a of deep-shaft reactor 30 and/or to a retention chamber 80 via return filtrate line 98. Deep-shaft reactor 30 is further fluidly connected with retention chamber 80. Retention chamber 80 is connected to deep shaft reactor 30 via a retention chamber outlet line 84 which connects an outlet of retention chamber 80 with one or more injection inlets of deep shaft reactor 30. Biomass extraction unit may be fluidly connected with retention chamber 80 via return filtrate line 98, whereby filtrate produced in biomass extraction unit 90 may be combined with feed gas comprising CO and saturated with CO in retention chamber 80 prior to recycle to reactor 30. In embodiments, a reactor outlet line 82 may connect reactor 30 with retention chamber 80. In such embodiments, reactor outlet line 82 may be configured for removal of a portion of suspension from a lower portion (for example, the lower 20%) of deep-shaft reactor 30. In such embodiments, a portion of suspension extracted from reactor 30 via reactor outlet line 82 may be combined with feed gas comprising CO via line 102 and introduced into retention chamber 80, wherein the extracted suspension may be saturated with CO prior to introduction into reactor 30. Retention chamber 80 is further fluidly connected with plasma gasification subsystem 100, for example, via a fermentation feed gas line 102.

[0039] Via the disclosed WTE method, carbon monoxide produced via plasma gasification is converted to hydrogen via net biological water shift reaction. The product hydrogen may be sold or converted to useful product, i.e. used to create electricity, used in the formation of a desired chemical product and/or recycled within the system as described in more detail hereinbelow.

I. Gasifying Waste Materials to Produce Synthesis Gas

[0040] The Waste to Energy method 10 comprises (I) gasifying a feed material comprising waste to produce gasifier gaseous product comprising synthesis gas. As depicted in Figure 1, (I) gasifying a feed material comprising waste, coal, wood chips, biomass, or other carbon source to produce gasifier gaseous product comprising synthesis gas may further comprise: (IA) introducing oxidant and gasifier feed comprising waste material to gasifier; and (IB) processing gasifier gaseous product. Processing gasifier gaseous product (IB) may comprise

one or more of: removing heat from gasifier gaseous product; removing particulate matter from gasifier gaseous product; and cleaning up gasifier gaseous product.

IA. Introducing Oxidant and Gasifier Feed Comprising Waste Material to Gasifier

[0041] Gasifying a feed material comprising waste to produce gasifier gaseous product comprising synthesis gas may comprise introducing oxidant and gasifier feed comprising waste material to a gasifier. Figure 3 is a schematic a schematic of an upstream gasification zone 100a suitable for use in carrying out portions of stage (I) of method 10. Upstream gasification zone 100a comprises gasifier 105.

[0042] Feed material comprising waste may be selected from coal fines, coal mine waste, biomass (forestry products corn stover, bagasse, switchgrass, miscanthus, etc.), municipal solid waste, industrial sludge (liquid and/or solid), auto shredder residue, petcoke, heavy oil sludge, refinery tar, wood chips, used plastics, tires, and combinations thereof. In embodiments, the feed material comprising waste is selected from agricultural waste, forestry waste, biomass, municipal solid waste, auto shredder residue, yard waste, industrial waste, and combinations thereof. In embodiments, the feed materials comprising waste is selected from biomass including, but not limited to, municipal solid waste (MSW); biosolids including manure; timber and wood waste; yard waste, corn stover, bagasse, miscanthus, switchgrass, corncobs, cotton plants, rice straw and other agricultural residues. In embodiments, the feed materials comprising waste include non-biomass waste selected from auto shredder residue including tires, paper, construction debris, furniture, auto fluff, auto shredder residue (ASR) and used plastics. Gasification of carbon-containing feed materials may be more environmentally-friendly than combustion thereof.

[0043] Feed material comprising waste may be introduced along with suitable oxidant into a gasifier 105. Gasifier 105 may be a plasma gasifier, e.g. a plasma gasification vitrification reactor (PGVR), available through Westinghouse Plasma Corporation (a division of Alter Nrg, Madison, PA). Alternatively, gasifier 105 may be any plasma gasifier capable of producing synthesis gas via gasification of a carbon-containing feed material comprising waste with a gasifier process gas.

[0044] Gasifier 105 converts the feed material comprising waste to gasifier gaseous product comprising synthesis gas. Gasifier 105 may comprise one or more plasma torches 140. Desirably, feed materials are gasified via production of superheated gas by plasma torch(es) 140 at temperatures in the range of from about 1,500°C to 5,500°C (2,732°F to 10,000°F). In applications, feed materials comprising waste are gasified at temperatures of greater than about 2200°C (3,992°F), alternatively greater than about 5000°C (9,032°F), or alternatively

greater than 5500°C (10,000°F), such that inorganics are liquefied. Vitrification may be induced to produce a non-hazardous glassy slag residue. Gasification may be performed such that low emissions of undesirable components such as NO_x, SO_x, tars, fly ash, dioxins, and/or furans are produced. Gasification may be performed at substantially atmospheric pressure.

[0045] The one or more plasma torches 140 of gasifier 105 may be positioned within a lower portion 117 of gasifier 105, whereby plasma heated gas from plasma torch(es) 140 enters gasifier 105 and rises. Lower portion 117 of gasifier 105 may comprise the lower ⅓ of gasifier 105. Gasifier 105 may be configured for operation at low gas velocity such that particulate carryover is low.

[0046] Feed materials comprising waste are introduced via one or more gasifier feed inlets 120 and feed lines 125 into gasifier 105. The feed materials may be introduced within the top half of gasifier 105, whereby the feed falls by gravity. In applications, the feed materials comprising waste are dried/heated prior to introduction into gasifier 105, as discussed further hereinbelow with respect to Figure 4. However, when gasification is performed at extreme temperatures, such heating and/or drying of the feed materials comprising waste may not be employed.

[0047] Within a gasification zone 115a of gasifier 105, gasification of gasifier feed with oxidant occurs. Oxidant may be introduced into gasifier 105 via one or more gasifier process gas inlets 180 positioned within gasification zone 115a. The gasifier process gas may comprise air, oxygen-enriched air, or substantially pure oxygen. Utilization of substantially pure oxygen or oxygen-enriched air as oxidant is desirable in applications where a low nitrogen content and/or increased synthesis gas content of the gasification product gas is desired. Water and/or flux may be introduced into gasifier 105 to enhance formation of vitreous product from melted ash and assist in slag withdrawal (i.e., adjust slag viscosity). The flux may be, for example, limestone.

[0048] Following gasification, gasifier gaseous product rises within gasifier 105 and enters a freeboard zone 115b above gasification zone 115 a. During passage through the freeboard zone (depending on the residence time), any ungasified solids fall back into the gasification zone 115a. Freeboard zone 115b may extend from about the level of the one or more gasifier feed inlets 120 to substantially the top 116 of gasifier 105 or to about the level of gasifier product gas outlet 130.

[0049] Gasifier gaseous product may be extracted from gasifier 105 via one or more gasifier product outlets 130 and gasifier gaseous outlet lines 135. Gasifying feed materials comprising waste may produce a gasification product gas comprising synthesis gas (hydrogen

and carbon monoxide) and a variety of other components depending on the gasifier feed material, the operation of the gasifier(s) (temperature, pressure, residence time, etc.), and the specific capabilities of the gasifier 105 utilized. For example, gasifier gaseous product comprising synthesis gas may further comprise carbon dioxide, nitrogen, ash, methane, ethane, water vapor, tar and/or ash along with trace amounts of components such as SO_x, NO_x, and H_2S. The gasifier gaseous product comprising synthesis gas may exit the gasifier 105 with a temperature in excess of 900°C, alternatively greater than or about 910°C. In applications, gasification of feed materials comprising waste is operated to produce synthesis gas in the gasifier gaseous product having a ratio of hydrogen to carbon monoxide of at least about 0.8; alternatively at least about 0.9; alternatively at least about 0.95.

[0050] Below gasification zone 115a is desirably a slag zone, from which ungasified metal and slag or vitrified product (depending on operating temperatures) are extracted from gasifier 105. For example, solids outlet 150 may be positioned within slag zone 115c and may be connected to solids outlet line(s) 155. Ideally, materials removed from slag zone 115c are environmentally friendly vitrified products which do not leach undesirable components into the environment. Gasification of feed material comprising waste may produce a glass-like slag which passes EPA-mandated Toxicity Characteristic Leachate Procedure (TCLP) requirements. Such vitrified materials may be sold, for example, as construction building materials, road fill, or may be safely landfilled.

[0051] Each plasma torch 140 may be configured to produce a superheated gas from a plasma process gas. The process energy is provided by direct heat transfer from an electric arc. Plasma is a scientific term referring to the fourth state of mater which is a very high temperature, ionized, conductive gas created within plasma torch 140 by the interaction of a plasma torch process gas with an electric arc. The plasma state exists within the arc within plasma torch 140. Upon exit from torch 140, the gas exists mainly in its neutral (nonionic, non-plasma) state.

[0052] Process gas may be supplied to plasma torch 140 via a plasma torch process gas supply system which may comprise a gas compressor, gas storage, or both. The plasma torch process gas may be any of a variety of reducing, oxidizing, and inert gases. Plasma torch 140 may produce a self-stabilized plasma arc and may produce a non-transferred arc. Power may be supplied to plasma torch 140 via a power supply system. The power supply system may comprise a thyristor power supply system for provision of DC power to plasma torch 140. Electrodes within plasma torch 140 may be cooled via a cooling water system 141 associated therewith. The plasma torch may be cooled with high pressure cooling water.

Process parameters and operation of the power supply system, the water cooling system, and the plasma process gas supply system may be controlled with a control system in communication with plasma torch 140.

IB. Processing Gasifier Gaseous Product

[0053] Gasifying waste materials to produce synthesis gas may further comprise (IB) processing gasifier gaseous product. Figure 4 is a schematic illustration of a downstream gasification zone 100b suitable for processing gasifier gaseous product. Processing gasifier gaseous product may comprise one or more of: removing heat from the gasifier gaseous product, removing particulate matter from the gasifier gaseous product, and cleaning-up the gasifier gaseous product to provide a fermentation feed gas comprising synthesis gas of a desired composition.

[0054] As (II) comprises biologically converting carbon monoxide in a fermentation feed gas comprising synthesis gas into fermentation product gas comprising hydrogen via fermentation, the temperature of the fermentation feed gas must be below the temperature at which the gasifier gaseous product exits gasifier 105. For example, the microorganisms utilized for biological conversion may operate most efficiently (produce significant hydrogen from CO and water) at temperatures of less than 70°C, less than 50°C, or less than 40°C. Therefore, processing gasifier gaseous product may include removing heat from the gasifier gaseous product.

[0055] Gasifier gaseous product may be introduced via gasifier product outlet line 135 into an oxidant preheater 165. In this manner, gasifier process gas introduced into gasifier process gas inlets 180 of gasifier 105 may be preheated as desired prior to introduction into gasifier 105. Although not shown in the embodiment of Figure 4, if desired, a portion of the heat in the gasifier gaseous product may be utilized for drying the gasification feed materials (e.g., biomass sludge) prior to introduction into gasifier 105 via gasifier feed inlet line 125. Process gas preheater 165 may be any suitable heat transfer reactor. For example, process gas preheater 165 may be a heat exchange-type reactor, configured such that process gas travels through, for example, tubes of the heat exchange-type reactor 165 and heat is transferred indirectly from the gasifier gaseous product in line 135 to a gasifier process gas.

[0056] Oxygen-enriched air or oxygen for use as oxidant may be produced from air via an oxygen-enhancement unit 166. Oxygen enhancement unit 166 may be any unit suitable for providing oxygen or oxygen-enhanced air for use in plasma gasifier 105. For example, oxygen-enhancement unit 166 may be an air separation unit, in which case the gasifier process gas comprises substantially oxygen. Alternatively, oxygen-enhancement unit 166

may comprise an oxygen pressure swing adsorption unit, in which case the gasifier process gas may comprise oxygen-enriched air, for example, 90% oxygen. Air is introduced into oxygen enhancement unit 166 via an air inlet 163, nitrogen or nitrogen-rich air is removed from oxygen-enhancement unit 166 via an outlet 164, and oxygen-enriched air (or substantially pure oxygen, in the case of an air separation unit) is removed from oxygen-enrichment unit 166 via an outlet 160.

[0057] Processing gasifier gaseous product (IB) may further comprise removing particulate matter from gasifier gaseous product. Particulate matter may be removed from gasifier gaseous product by, for example, centrifugation, electrostatic precipitation, filtering, or a combination thereof. Downstream gasification zone 100b may further comprise a particulate removal device 175. Particulate removal device 175 may be directly connected with product outlet line 135 of gasifier 105 or, alternatively, may be connected with process gas preheater 165 via a reduced-temperature gasification product line 170. Particulate removal device 175 may be any suitable apparatus capable of removing ash and other particulate matter from the temperature-reduced gasification product in line 170 or gasifier gaseous product in gasifier outlet line 135. For example, particulate removal device 175 may be a cyclone, an electrostatic precipitator, a baghouse, or any other suitable device known to those of skill in the art. Within particulate removal device 175, particulate material is separated from the gas introduced therein. Particulate matter may be removed from particulate removal device 175 via an outlet 185, and particulate-reduced gasifier gaseous product may be removed via an outlet line 190.

[0058] Further heat may be extracted from the gasifier gaseous product via generation of steam. For example, downstream gasification zone 100b may further comprise heat recovery unit 195. Heat recovery unit 195 may be any apparatus suitable for the transfer of heat from particulate-reduced gasification product in line 190, for example a heat recovery steam generator or HRSG. Water or other suitable heat transfer fluid may be introduced into heat recovery unit 195 via a coolant inlet 215, and passed through one or more heat transfer coils 217. Within heat recovery unit 195, heat is transferred from gas introduced therein (i.e., the particulate-reduced gasification product) to, for example, the heat transfer fluid within the coil(s) 217 of heat recovery device 195. Steam produced within heat recovery unit 195 may be introduced into a steam turbine 218 via a steam outlet 216 of coil(s) 217. Electricity may be generated by steam turbine 218. Alternatively, steam produced via heat recovery unit 195 may be used during cleaning of deep-shaft reactor 30, as described further hereinbelow. Electricity 95a produced from the hot gasifier gaseous product may be used throughout WTE

system 10a, for example, for running oxygen-enhancement unit 166 and/or hydrogen upgrading unit 112, or may be utilized in another associated part of system 10a or sold for profit.

[0059] Processing gasifier gaseous product may further comprise cleaning-up the gasifier gaseous product to provide a fermentation feed gas comprising synthesis gas of a desired composition. Depending on the gasifier feed materials introduced into gasifier 105 via gasifier feed inlet 125, operation and configuration of gasifier 105, the particulate-reduced/temperature-reduced gasification gas will comprise various components in addition to synthesis gas. Depending on the desired composition of the resultant synthesis gas, downstream gasification zone 100b may further comprise one or more synthesis gas clean-up units 210. The one or more synthesis gas clean-up units 210 may be configured to remove non-synthesis gas components from the gas introduced therein, e.g., the particulate-reduced/temperature-reduced gasification gas from heat recovery device 195. Any synthesis gas clean-up units known in the art may be utilized, for example, acid gas removal units may be used to remove extraneous carbon dioxide. Such removed carbon dioxide may, depending on plant locations, be sold for purposes such as enhanced oil recovery operations. Thus, in applications, particulate-reduced/temperature-reduced gasification gas is removed from heat recovery device 195 via an outlet line 200 and introduced into one or more synthesis gas clean-up units 210.

[0060] At least a portion of the synthesis gas produced via gasifying feed materials comprising waste is biologically converted into hydrogen via the disclosed method. Downstream gasification zone 100b may comprise an outlet line 102 whereby cleaned-up synthesis gas is introduced into a deep shaft fermentation reactor as discussed further hereinbelow. The cleaned-up synthesis gas comprises CO and the levels of other gaseous components are desirably not unduly toxic to the microorganisms selected for biological conversion.

[0061] Gasification may thus be performed such that a desired synthesis gas is produced having a desired composition and a desired temperature. The operation of plasma torch 140 (i.e., the power provided thereto), the gasification feed material selected and introduced into the gasifier, and/or the oxidant utilized in gasifier 105 may be chosen to produce synthesis gas of a desired composition (H_2:CO ratio, N_2 content, etc). A downstream gasification section 100b may be used to achieve the desired temperature of the gasification-produced synthesis gas.

[0062] It should be noted that processing gasifier gaseous product may comprise a variety of processing steps and may be performed via a variety of systems. For example, heat removal may comprise transferring heat to gasifier process gas, to feed material comprising waste, and/or producing steam. Depending on the quality of the gasifier gaseous product, synthesis gas clean-up may not be required. Also, removal of particulate matter may be performed before and/or after heat removal and synthesis gas clean-up. As such, a downstream gasification zone 100b may not comprise each and every unit described in relation to Figure 4, and the order of the devices may be varied. For example, in some applications, synthesis gas clean-up unit(s) 210 may not be required, a particulate separation device 175 may be positioned upstream of heat recovery device 195, or process gas preheater 165 may be absent.

II. Biologically Converting CO in a Fermentation Feed Gas to Produce a Fermentation Product Gas Comprising Hydrogen

[0063] WTE method 10 further comprises (II) biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen, wherein at least a portion of the carbon monoxide is obtained from the gasifier gaseous product. Biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen may comprise: (IIA) providing a reactor (e.g., a deep shaft reactor DSR) comprising activated suspension; (IIB) saturating a fluid with CO from the fermentation feed gas comprising CO; (IIC) introducing CO-saturated fluid into the reactor; and (IID) removing fermentation product gas comprising hydrogen from the reactor.

Overview

[0064] Biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen is performed by microorganisms which utilize carbon monoxide as a food source, thereby producing hydrogen via the net water gas shift (water-gas splitting reaction):

$$CO + H_2O \rightarrow CO_2 + H_2. \qquad (1)$$

[0065] The reaction of Equation (1) is mediated by proteins coordinated in an enzymatic pathway, and takes place at ambient temperature and pressure, with the thermodynamic equilibrium (desirably for the production of hydrogen) to the right of Eq. (1).

[0066] Biological conversion may comprise: suspending microorganisms capable of carrying out the water-gas splitting reaction in Eq. (1) in an aqueous nutrient medium initially lacking a carbon source, exposing at least a portion of the suspension to a light source to activate a metabolic pathway that includes the water-gas shift reaction (1), and then

incubating anaerobically in a slow-flowing, carbon monoxide-depleted stream within a downcomer section of reactor 30.

[0067] A fluid is saturated with carbon monoxide in the feed gas comprising monoxide and the saturated fluid is injected into reactor 30 in such a manner that injection of the CO-saturated fluid thereto creates/maintains a fast-flowing, carbon monoxide-rich stream within a riser section 70 of reactor 30. The fluid saturated within retention chamber 80 may be at least a portion of return filtrate from biomass extraction unit 90, as indicated in the embodiment of Figure 5, and/or a portion of the CO-starved microorganisms from downcomer 50 of reactor 30, as indicated in the embodiment of Figure 6. Retention chamber 80 external to reactor 30 provides a CO-saturated filtrate or CO-saturated suspension according to Figures 5 and 6, respectively.

[0068] Following contact with CO-saturated fluid, metabolically activated microorganisms in the CO-enriched fast flow zone of riser 70 metabolize the CO-saturated medium to form fermentation product gas including hydrogen and carbon dioxide. Gas coming out of solution while in the riser 70 creates a gas-lift pump, which enhances circulation of the suspension throughout reactor 30 from the fast-flowing phase within the riser section 70 of reactor 30 back to the slow-flowing phase within the downcomer 50 of reactor 30. Product hydrogen, and other undissolved gas, enters a gaseous headspace 44 above the suspension level 43 of reactor 30 prior to return of the suspension to the downcomer 50.

[0069] In embodiments, the majority of the biological conversion is performed in the absence of substantial light. In embodiments, biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen is performed substantially anaerobically.

IIA. Providing A Reactor Containing Photo-activated Suspension

[0070] Biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen (II) may comprise (IIA) providing activated suspension of microorganisms adapted for CO fermentation. The suspension may be provided in a reactor. The reactor may be a deep shaft reactor. Figure 5 is a schematic of a WTE system 10a depicting a suitable deep-shaft reactor 30 and relation thereof to hydrogen recovery system 110, biomass separation unit 90, retention chamber 80, and plasma gasification subsystem 100 according to an embodiment of this disclosure.

DSR 30

[0071] Deep-shaft reactor 30 may be configured as a vessel having a top 12a, a bottom 12b, and walls 33. Deep shaft reactor 30 may be an open-ended pressure vessel. The head of

pressure provided by the suspension during operation serves to provide pressure variation along the length of the vessel, and promotes circulation of suspension.

[0072] In applications, reactor 30 is cylindrical. In certain embodiments, reactor 30 has a long axis L1 oriented vertically between the top 12a and the bottom 12b. In some embodiments, the length L1 to be used for a particular application is optimized based on the pressure sensitivity of the microorganism(s) to be used in reactor 30, and such other factors as CO or CO_2 toxicity at various pressures.

[0073] In applications, long axis L1 is in the range of from about 10m and about 600m, alternatively in the range of from 50m to 600m. In preferred embodiments, deep-shaft reactor 30 has a long axis L1 of greater than about 50m. In applications, L1 may be about 150 meters (492 ft) in some cases. Deep shaft reactor 30 has a short axis D, perpendicular to long axis L1. Short axis D is the diameter of the vessel in cylindrical embodiments. Reactor 30 may be of non-cylindrical shape, such as, without limitation, rectangular, or polygonal. Deep shaft reactor 30 has a long axis L1 that is at least twice the dimension of the short axis D. In some embodiments, inner diameter D of reactor 30 is up to 6 meters (20 ft), and reactor length L1 is up to 600 meters (2000 ft). Head 40 of reactor 30 may comprise at least a portion of spillover zone 16a, a headspace 44, and illumination assembly 46. Head 40 may extend a distance L5 outward from walls 33 of reactor 30. In this manner, an annular suspension region 48 at the top of reactor 30 may be defined. Such an annular suspension region may be conducive to transfer of product and evolved gases from the suspension in annular suspension region 48 into headspace 44 and subsequent removal therefrom via hydrogen removal system 110, as further described hereinbelow. Such an annular suspension region, by providing a larger surface area of interaction between headspace 44 and annular region 48, may be configured to enhance exposure of the circulating suspension to light during activation, prior to downward flow into the darkened slow-flow zone 50 of reactor 30. By increasing the diameter, the surface area for light activation and for de-gassing may be increased. Alternatively, the head 40 of reactor 30 has the same diameter D as the shaft defined by walls 33. In some embodiments, reactor head 40 is made to be detachable from deep shaft reactor 30.

[0074] Annular region 48 of reactor head 40 may be fitted with a baffle configured to encourage suspension emerging from riser 70 to traverse a substantial horizontal distance along annular region 48, and facilitate release of H_2 product into headspace 44 prior to descent of gas-disengaged suspension slowly in downcomer 50, wherein the suspension (again) becomes CO depleted.

[0075] Head 40 includes one or more inlets 41 for introducing nutrients, microorganisms, sterile fresh water injection, sterile recycled filtrate, pH adjusting agents, and other materials into reactor 30. For example, in the embodiment of Figure 5, head 40 comprises inlet 41a for a water stream comprising fresh and recycled water, an inlet 41b for nutrients, an inlet 41c for fresh microorganisms, and an inlet 41d for chemicals (e.g., pH adjusting base). Lines 41a, 41b, 41c, and 41d may be utilized during start-up (and optionally thereafter) to introduce water, nutrients, selected microorganisms, and chemicals to a temperature-controlled reactor 30 to prepare (maintain) a biomass suspension. Although depicted at the top of reactor 30, it is envisioned that inlets 41a-41d may connect through any position of head 40 or walls 33.

[0076] In applications, deep-shaft reactor 30 is disposed below ground level G, for instance in a shaft, borehole, or other vertically oriented compartment in the earth. Alternatively, reactor 30 is at least partially above ground level G. Reactor 30 may be surrounded by a cooling chamber 11, as described further hereinbelow. Furthermore, an insulation layer (not shown) may be positioned between at least a portion of the surrounding soil and reactor 30. Such an insulation layer may be made of polyurethane and may be positioned within a borehole prior to positioning of the reactor 30 within the borehole, concomitant with positioning of reactor 30 into the borehole, or after placement of reactor 30 within the borehole.

[0077] Walls 33 and bottom 12b of reactor 30 are constructed of any corrosion resistant material and are desirably constructed of a thermally-conductive material. In certain embodiments, the walls 33 and bottom 12b of deep shaft reactor 30 are constructed of aluminum, or stainless steel. The interior of reactor walls 33, the bottom 12b of reactor 30, divider 34, and any parts exposed to bacterial suspension during operation may be made of polished steel or other suitable material or may be clad therewith, such that adhesion and growth of bacteria thereon is discouraged. Reactor 30 comprises any suitable vessel for carrying out (II) biological conversion of CO from synthesis gas to fermentation product gas comprising hydrogen. In embodiments, reactor 30 is a pressurized vessel, reactor, container or the like configured to contain a fermentation reaction.

[0078] Deep shaft reactor 30 further comprises divider 34. In certain instances, divider 34 is a virtual division, wherein the normal operating suspension volume is a unitary volume. In such embodiments, divider 34 is an axis of circulation about which the liquid volume within reactor 30 circulates. Divider 34 may comprise a region of shear, such that fluid flowing downward and fluid flowing upward interact at the interface thereof.

[0079] Generally, divider 34 will be a physical divider, such as a baffle, wall, or other structure within reactor 30 which serves to direct or control liquid phase flow. Divider 34 may be oriented in any direction with respect to long axis L_1 of reactor 30. In embodiments, divider 34 is oriented vertically, parallel to long axis L_1. Divider 34 extends from a distance L3 below suspension level 43 to a distance L4 above bottom 12b of reactor 30. In embodiments, divider 34 is substantially parallel to long axis L_1 and perpendicular to short axis D. Divider 34 divides the operating reactor volume into a fast-flow or riser section 70 and a slow-flow or downcomer section 50. Riser section 70 and downcomer section 50 may be of about equal volume. Alternatively, the volume and/or cross-sectional area of downcomer section 50 is greater than about the volume/cross-sectional area of riser section 70, to promote relatively slower flow in downcomer 50 relative to riser 70.

[0080] A schematic horizontal cross section view of an embodiment of a deep shaft reactor 230 configured as described in Figure 5 is shown in Figure 7a. Reactor walls 233 enclose one slow-flow zone 250 and one fast-flow zone 270. The slow- and fast-flow zones are divided by a partition or wall 234, which is positioned so that the volume of slow-flow zone 250 is greater than the volume of fast-flow zone 270. In another embodiment, the bioreactor of Figure 5 is configured as illustrated in Figure 7b. A horizontal cross section of a deep shaft reactor 330 is shown which includes two fast-flow zones 370a, 370b located on opposite sides of reactor 230 and enclosed by reactor walls 333. One slow-flow zone 350 is disposed between the two fast-flow zones 270a, 270b.

[0081] A spillover region 16a located proximal suspension surface 43 has a vertical height L3 and width D (or part D + L5 in embodiments with annular region 48). Spillover region 16a is configured to allow suspension circulation during operation (indicated by the dashed arrows) to proceed over or around divider 34 between riser 70 and downcomer 50. Similarly, flow-through region 16b having a vertical height L4 and width D, that is configured such that circulation (indicated by dashed arrows) continues under, or around divider 34 between riser 70 and downcomer 50. Divider 34 is designed such that circulation of suspension within reactor 30 proceeds in any direction such that reactant suspension in reactor 30 is circulated continuously from an upper region of downcomer 50 to a lower region of downcomer 50 to a lower position within riser 70 to a higher position within riser 70, passing around divider 34, from downcomer 50 to riser 70.

[0082] Providing activated suspension of microorganisms adapted for CO fermentation (IIA) may comprise introducing microorganisms, fermentation medium, water, and nutrients into a temperature-controlled DSR 30 as described above. Although a deep shaft reactor 30 is

described, any other suitable reactor may be employed within WTE system 10a. Such a suitable reactor should be configured for the following: handling large volumes of CO gas (e.g., in the range of 3000 kg/h to over 10000 kg/h of fermentation feed gas; alternatively greater than about 5,000 kg/h), promoting excellent gas to liquid transfer rates, allowing effective control of gas injection control, control, operating at high pressures, allowing for effective cleaning to avoid contamination (*e.g.*, contamination with undesirable microorganisms), temperature control, construction using common, standard parts for easy servicing/maintenance and economy of construction, explosion-resistance, ability to run continuously, and effective mixing throughout the reactor volume.

Reactor Suspension

[0083] The suspension may comprise any suitable microorganism known in the art to consume carbon monoxide under aqueous anaerobic conditions and release H_2 according to the reaction portrayed in Equation (1). In embodiments, the suspension comprises thermophilic *Carboxydothermus hydrogenoformans Z-2901*; *Rubrivivax gelatinosus*; or *Rhodospirillum rubrum*. These microbes can be obtained from microbial banks such as ATTC. Some additional bacteria that are potentially suitable for production of hydrogen with the disclosed system include *Bdellovibrio sp.*, *Rhodopseudomonas palustris*, *Rhodobacter sphaeroides*, *Citrobacter sp. Y19, Methanosarcina acetivorans c2A, and Bacillus smithii.*

[0084] The suspension may comprise any suitable growth medium for the selected microorganisms may be used, provided that it lacks a carbon source. One such growth medium contains RCVBN medium modified to omit a carbon source (Maness, *et al.* Appl. Environ. Microbiol. 2002. 68:2633-2636).

[0085] Other microorganisms that are capable of fermenting CO to produce H_2 may be utilized to provide the suspension; such microorganisms may be identified by screening candidate microorganisms to identify (1) efficiency of CO fed to H_2 produced; (2) variation of CO toxicity with pressure; (3) variation of CO toxicity with CO concentration; (4) optimum operating temperature; (5) optimum nutrient dosing; (6) optimum operating pH; (7) sensitivity to SOx and NOx contaminants in CO feed gas; and (8) ease of removal from reactor during cleaning.

[0086] Biologically converting (II) may be performed at pressures (depths of reactor 30) and temperatures suitable for optimum conversion of CO to hydrogen by the selected microorganisms. In instances, operating temperatures are less than 35°C to achieve maximal hydrogen production. In applications, biological conversion is performed at an operating temperature in the range of from about 30°C to 70°C. Alternatively, biological conversion is

performed at a temperature in the range of from about 35°C to 50°C. In some cases the operating biological conversion temperature is in the range of about 37–53°C. Alternatively about 37°C. The microorganisms may have a preferred pH operating range. As mentioned above, pH adjustment inlet line(s) 41c and a pH measuring and control system may be utilized to maintain a desired pH of the suspension within reactor 30. In embodiments, the pH control system is used to maintain a pH in the range of from about 7.5 to about 9.5; alternatively, about 9.

[0087] The activated suspension may be introduced into a suitable reactor filled to a normal operating fill line 43. Normal operating suspension level 43 is a vertical distance L2 from bottom 12b of reactor 30. Normal operating suspension level 43 defines a normal reactor suspension volume, defined as the volume of suspension contained within reactor walls 33, reactor bottom 12b, and normal operating suspension level 43 during operation of reactor 30. For the embodiment of Figure 5, the normal operating suspension volume is $\pi (D/2)^2 L_2$. The operating suspension volume of deep shaft reactor 30 may be between about 50% and about 99% of the total internal volume of reactor 30. Normal operating suspension level 43 comprises a suspension/gas interface within reactor 30 during operation. Level meters may be utilized to maintain the suspension at about the normal operating fill level 43 during (II) biological conversion of CO.

Photoactivation

[0088] The suspension may be photoactivated by exposing at least a portion of the suspension within the DSR to light. DSR 30 may comprise a head 40 comprised of (from lowest to highest in elevation) annular suspension region 48, headspace 44, and illumination assembly 46. Illumination assembly 46 may be concealed into the roof (*i.e.*, uppermost region of head 40) of reactor 30 to avoid chemical and humidity damage during operation, while ensuring transmittance of an appropriate wavelength light to suspension in spillover region 16a. Illumination system 46 may be used to photoactivate the hydrogen-producing bacteria during start-up or bacterial replacement within reactor 30. Illumination assembly 46 may comprise one or a plurality of lamps, for example, one or more incandescent lamps.

[0089] Illumination assembly 46 is operable to photoactivate the selected microorganisms and initiate a biological pathway that includes the water-gas shift reaction (1). After an initial exposure of the suspension to illumination effective to stimulate the photosynthetic CO oxidation pathway in the microorganisms, the activated microorganisms may then be grown in darkness, especially when the microorganisms are known to consume hydrogen in the presence of light.

[0090] Suspension may be photoactivated by exposing suspension in annular liquid region 48 to light in the visible wavelength range via illumination assembly 46. The duration of light exposure for activation may be controlled as desired via control apparatus based on the parameters of a given application, such as flow rate of the suspension, the intensity of the light, and the exposed surface area of the suspension in head 40.

[0091] Although fermentation of CO by the water-gas shift reaction will continue in the presence of light, it is thought that endogenous hydrogenases will oxidize the produced H_2 to support light-dependent CO_2 fixation. Therefore, reactor 30 may be operable in an absence of light following activation, to enhance the yield of H_2 product.

[0092] In embodiments, illumination assembly 46 is located external to reactor 30 such that activation of selected microorganisms may be performed prior to introduction of microorganisms into reactor 30.

[0093] Referring again to Figure 5, in some instances, a photoactivation control system may be utilized to again expose fresh microorganisms introduced into reactor 30 via microorganism inlet 41c and/or suspension circulating from fast flow zone 70 through head 40 and downward into slow-flow zone 50 to visible light as it passes through head 40, to ensure activation of the CO oxidation pathway in the recirculated microorganisms and/or make-up microorganisms. The photoactivation control system may be designed such that non-initial exposure to light may be brief. Following such exposure, the control system may be designed to again expose the flowing suspension to darkness.

IIB. Saturating Fluid with Carbon Monoxide in Fermentation Feed Gas

[0094] Biologically converting CO from synthesis gas to fermentation product gas comprising hydrogen (II) further comprises (IIB) saturating fluid with carbon monoxide from the fermentation feed gas comprising carbon monoxide. The fluid saturated with carbon monoxide may be filtrate return water separated from biomass in biomass extraction unit 90, a portion of CO-deprived suspension extracted from a lower portion of downcomer 50, or a combination thereof.

[0095] During operation, activated microorganisms in the suspension are initially incubated in the dark under anaerobic, slow-flow, carbon-monoxide-depleted conditions ("CO-depleted conditions" to produce CO-starved suspension). During operation, suspension in downcomer 50 becomes CO-depleted, while that in the riser is CO-enhanced due to introduction of CO-saturated fluid from retention chamber 80 into riser 70. The desired biochemical reaction (*i.e.*, the water-gas shift reaction) benefits from a CO feed gas starvation, as food-deprived microorganisms are primed for enhanced metabolic activity upon restoration of a food

source (*i.e.*, carbon monoxide). The same benefit would not be achieved if feed gas were injected into a conventional batch fermentation mixture. Thus, in embodiments, the method comprises no direct introduction of feed source into the downcomer 50 of the deep shaft reactor. In embodiments, feed source may be injected in the lower part of the downcomer 50 to take advantage of the down ward motion to further compress the gas.

Saturating a Return Filtrate Water Portion of Biomass-Reduced Effluent with CO

[0096] Referring now to Figure 5, in embodiments the disclosed WTE method comprises saturating filtrate water with CO gas. The microorganisms of the suspension metabolize and proliferate, in some cases doubling in population after only two hours of processing. A desired level of total dissolved solids may be maintained within the reactor by continuously, periodically or semi-continuously removing a portion of suspension from the reactor. Furthermore, as the fermentation feed gas introduced into reactor 30 via fermentation feed gas inlet line 102 may comprise some dust and/or tar, it may be desirable to extract biomass to remove such materials which may accumulate in the biomass cell structure. Also, bicarbonate will be formed from the biologically-produced carbon dioxide due to utilization of suitable pH, as discussed hereinabove. Removal of at least a portion of suspension may facilitate dilution/removal of the bicarbonate. Thus, biologically converting CO into fermentation product gas comprising hydrogen (II) may further comprise removing all or a portion of the circulating suspension from the reactor to remove excess or spent microorganisms.

[0097] Microorganisms may be separated from the second portion of suspension to produce a sludge comprising separated microorganisms and a biomass-reduced effluent. In embodiments, (IIB) saturating fluid with carbon monoxide from the fermentation feed gas comprising carbon monoxide comprises saturating at least a portion of the biomass-reduced effluent with CO.

[0098] A biomass extraction unit may be utilized to separate excess biomass from the extracted portion of suspension. A suitable biomass extraction unit 90 may be positioned above ground level G, below ground level G, or a combination thereof. Spent biomass may be introduced via a spent biomass outlet line 89 from a location within the operating reactor volume of reactor 30, i.e., a location within reactor 30 below normal suspension fill line 43, into a biomass extraction unit 90. In embodiments, as shown in Figure 5, spent biomass is extracted from annular extension region 48 of reactor 30. The removal of at least a portion of the circulating suspension from reactor 30 may be periodic, continuous, or semi-continuous, or may vary depending on measured microorganism concentration within reactor 30. One or

more TDS (total dissolved solids) meters may be utilized to measure the TDS concentration within the reactor during operation. When the measured TDS is too high and/or replacement of biomass is desired, at least a portion of the circulating suspension may be extracted from the reactor and introduced into a biomass separation unit.

[0099] Aqueous medium is separated from spent bacteria in biomass extraction unit 90. Sludge comprising separated microorganisms and a biomass-reduced effluent are extracted from biomass extraction unit 90, for example, via an aqueous phase outlet line 92 and a sludge outlet line 91. Biomass separation may be performed by any suitable device or devices. Biomass separation may comprise utilization of a membrane bioreactor, centrifuge, decanter, and/or clarifier. Separation may be effected by filtration, centrifugation, or a combination thereof. To resist the likelihood of contaminant introduction into the reactor, the microorganisms may be separated from the extracted portion of suspension via ultrafiltration or microfiltration.

[00100] At least a portion of the biomass-reduced effluent may be recycled to the reactor. In this manner at least a portion of the water removed from reactor 30 via spent suspension outlet line 89 may be recycled for reuse within reactor 30 and the production of further hydrogen therefrom. The biomass-reduced effluent may be combined with fresh water, e.g. via fresh water line 94. Alternatively, fresh sterile water may be introduced into the reactor separately, e.g. via line 94 may introduce (not shown in the embodiment of Figure 5). Dilution with fresh sterile water may reduce the bicarbonate concentration. As mentioned above, a TDS meter may be utilized to measure the TDS within the suspension within reactor 30.

[00101] In embodiments, a portion of the biomass-reduced product from the biomass extraction unit 90 is recycled via return water line 98 and retention chamber 80 to reactor 30. In such embodiments, as depicted in Figure 5, the return water is combined with fermentation feed gas comprising carbon monoxide and introduced into retention chamber 80 and saturated with CO therein.

[00102] During biological conversion, the amount of water introduced into the reactor (e.g. via fresh water line 94, recycle water line 93 and water inlet 41a, and/or return water line 98) as well as the amount of nutrients, fresh microorganisms, and chemicals introduced into reactor (e.g. into reactor head 40 via inlet lines 41b, 41c, and 41d) may be controlled in response to the measured total dissolved solids or TDS within reactor 30, the level of suspension, or both. A desired TDS level may be in the range tolerable to the microbes and permitted by the department of environment discharge standards on TDS. Recycled effluent

from biomass extraction unit(s) 90 may be supplemented with fresh nutrients and sterile water as needed.

[00103] Sludge separated from the second portion of suspension (e.g. sludge in outlet line 91) comprises spent microorganisms. The sludge may be utilized in a variety of ways, for example, at least a portion of the sludge may be gasified for production of additional gasifier gaseous product comprising synthesis gas. Thus, at least a portion of the sludge may be recycled to gasifier 105. For example, sludge outlet line 91 may be fluidly connected to plasma gasifier 105 or gasifier inlet feed line 125 for carbon recycle. Alternatively, or additionally, a portion of the spent biomass extracted via sludge outlet line 91 may be disposed of as waste, in accordance with applicable regulations.

[00104] At least a portion of the portion of the spent biomass may be utilized as protein feed in husbandry operations, for example as proteinaceous cattle feed. If not contaminated, portions of the extracted biomass may be utilized to startup additional reactors, for example, when biological conversion is performed using a plurality of fermentation reactors in series, as discussed further hereinbelow. Sludge may be dewatered, for example, with one or more centrifuges (not shown in the embodiment of Figure 5).

[00105] Depending on the composition of fermentation feed gas comprising CO (which itself depends somewhat on the gasifier feed material), the suspension may comprise trace toxic elements such as, but not limited to, hydrogen sulfide, and nitrogen compounds such as NO_x. Although the levels of these contaminants in the fermentation feed gas may be low, with continuous operation, such contaminants may accumulate. Depending on the effect of such accumulated contaminants on the biomass, biological conversion may further comprise steps for reducing such contaminants from the extracted suspension via centrifuge system (biomass extraction unit 90).

[00106] Saturating fluid with carbon monoxide from the fermentation feed gas comprising carbon monoxide may comprise contacting, under pressure, at least a portion of biomass-reduced effluent from biomass extraction unit 90 with fermentation feed gas comprising CO in a retention chamber.

[00107] Saturating fluid with CO may thus comprise forming a mixture comprising at least a portion of biomass-reduced effluent and the fermentation feed gas (wherein at least a portion of the CO in the fermentation feed gas was obtained from gasifying carbonaceous feed materials such as waste) and increasing the pressure of the mixture of fermentation feed gas comprising CO and biomass-reduced effluent. The mixture may be formed using any means suitable for raising the pressure of the withdrawn effluent and/or combining the

biomass-reduced effluent with fermentation feed gas comprising CO, for dispersion of the fermentation feed gas therein.

[00108] As indicated in Figure 5, a pump 1h and venturi 85 may be used to draw biomass-reduced effluent from biomass extraction unit 90 and combine the removed effluent (or 'water filtrate') with fermentation feed gas comprising carbon monoxide via fermentation feed gas inlet line 102. Pump 1h and venturi 85 also provide pressure to the extracted biomass-reduced effluent drawn therein. Alternatively, the biomass-reduced effluent may be pumped into retention chamber 80 at pressure and mixed with fermentation feed gas comprising CO within retention chamber 80 (not shown in Figure 5). In such embodiments, CO-depleted mixture fermentation feed gas inlet line 102 may connect directly to retention chamber 80 in certain applications. Thus, gasification subsystem 100 may be coupled to retention chamber 80 indirectly via fermentation feed gas inlet line 102, venturi 85, and venturi outlet line 86. Alternatively, gasification subsystem 100 may be coupled directly to retention chamber 80 via line 102 (not shown as such in the embodiment of Figure 5), so that fermentation feed gas and withdrawn biomass-reduced effluent may be fed separately into retention chamber 80 and mixed therein. The utilization of a pump 1h and venturi 85 may be preferable over the use of a synthesis gas compressor, as synthesis gas is explosive and the fermentation feed gas comprising CO may also comprise hydrogen. Furthermore, the fermentation feed gas may be a synthesis gas comprising substantial ash and/or soot. In these applications, compression of the fermentation feed gas would be dangerous and expensive, although theoretically utilizable. Desirably, the venturi is utilized to provide sufficient vacuum to supply fermentation feed gas comprising CO to the reactor system.

[00109] Return water filtrate extracted from biomass-extraction unit 90 via return water line 98 is saturated with carbon monoxide feed gas, in retention chamber 80, as the dissolved carbon monoxide provides the necessary carbon source for the microorganisms to carry out the water-gas shift reaction (1) upon injection into reactor 30.

Saturating a Portion of CO-Depleted Suspension from Downcomer 50 with CO

[00110] In embodiments of the disclosed WTE method, saturating fluid with carbon monoxide from the fermentation feed gas comprising carbon monoxide comprises saturating a portion of CO-depleted suspension from a lower portion of the downcomer with CO. As indicated in the embodiment of Figure 6, a portion of CO-depleted suspension may be extracted from a lower portion (lower 20%, for example) of downcomer 50, for example, via CO-depleted suspension outlet line 82. In such embodiments, another portion of CO-depleted suspension is allowed to flow around the bottom of divider 34 and pass into riser 70

without exiting reactor 30. CO-depleted suspension may be extracted via vacuum, for example, via pump 1h.

[00111] CO-depleted suspension may be extracted adjacent flow-through zone 16b and/or bottom 12b of reactor 30. CO-depleted suspension may be extracted from a horizontal position within a lower portion of downcomer 50; the bottom of riser 70, below the lowest injection nozzle or sprayer 2g; or substantially therebetween. The extracted portion of CO-depleted suspension may be saturated with CO gas by contacting, under pressure, the extracted portion of CO-depleted suspension with fermentation feed gas comprising CO in retention chamber 80.

[00112] Saturating a fluid with CO may comprise forming a mixture comprising the extracted portion of CO-depleted suspension and the fermentation feed gas (wherein at least a portion of the CO in the fermentation feed gas was obtained from gasifying feed materials comprising waste) and increasing the pressure of the mixture of fermentation feed gas comprising CO and CO-depleted suspension. The mixture may be formed using any means suitable for raising the pressure of the withdrawn suspension and/or combining the removed CO-depleted suspension with fermentation feed gas comprising CO, for dispersion of the fermentation feed gas therein.

[00113] A pump 1h and venturi 85 may be used to draw CO-depleted suspension from reactor 30 and combine the removed CO-depleted suspension with fermentation feed gas comprising carbon monoxide via fermentation feed gas inlet line 102. Pump 1h and venturi 85 also provide pressure to the extracted CO-depleted suspension drawn therein. Alternatively, the CO-depleted suspension may be pumped into retention chamber 80 at pressure and mixed with fermentation feed gas comprising CO within retention chamber 80. In such embodiments, CO-depleted mixture fermentation feed gas inlet line 102 may connect directly to retention chamber 80 in certain applications. Thus, gasification subsystem 100 may be coupled to retention chamber 80 indirectly via fermentation feed gas inlet line 102, venturi 85, and venturi outlet line 86. Alternatively, gasification subsystem 100 may be coupled directly to retention chamber 80 via line 102 (not shown as such in the embodiment of Figure 5), so that fermentation feed gas and withdrawn CO-depleted suspension may be fed separately into retention chamber 80 and mixed therein.

[00114] As mentioned above, the utilization of a pump 1h and venturi 85 may be preferable over the use of a feed gas compressor, as synthesis gas is explosive and the fermentation feed gas comprising CO may also comprise hydrogen. Furthermore, the fermentation feed gas may be a synthesis gas comprising substantial ash and/or soot. In these

applications, compression of the fermentation feed gas would be dangerous and expensive, although theoretically utilizable.

[00115] In embodiments as depicted in Figure 6, extracted CO-starved suspension is saturated with carbon monoxide feed gas, in retention chamber 80.

[00116] Saturation of fluid with fermentation feed gas comprising CO is designed to reduce gas mass transfer limitations within the system and enhance reaction rate within reactor 30. Retention chamber 80 may be positioned either above ground level G, below ground level G, or may be split therebetween.

[00117] The fluid spends a retention time within retention chamber 80 such that the fluid is exposed to saturated with CO from the fermentation feed gas comprising CO. Saturation of fluid with CO may occur substantially in darkness. The theory of operation is that, as the suspension is CO-depleted upon entry into riser 70 of reactor 30, the organisms will super activate after starvation, and subsequently produce hydrogen more efficiently. The activated microorganisms in the CO-enriched fast flow region of the riser 70 the will produce H_2 and CO_2 from the carbon monoxide dissolved into the fluid during the time spent within retention chamber 80.

[00118] The metabolic process by which H_2 is generated may occur in retention chamber 80 (in embodiments in which suspension is introduced therein), during transfer from retention chamber 80 to riser 70 of deep shaft reactor 30, and during circulation through fast-flow zone 70. A majority of the hydrogen production may be expected within riser 70 (especially in instances wherein return water filtrate is saturated with CO in retention chamber 80). The production of H_2 may also occur as the suspension circulates through the lower portion (annular liquid region 48) of reactor head 40

[00119]

IIC. Introducing CO-Saturated Fluid to the Reactor

[00120] Biologically converting CO from synthesis gas produced via gasification of waste (II) further comprises (IIC) introducing CO-saturated fluid into the riser of the reactor such that the suspension within the reactor circulates about the divider flowing with a first linear velocity up the riser, passing over the top of the divider, and flowing with a second linear velocity down the downcomer, wherein the first linear velocity is greater than the second linear velocity.

Injection System and Control

[00121] CO-saturated fluid may be introduced into the riser of the reactor via an injection system. During cleaning operations, this injection system may also be utilized to

clean the portions of the fermentation reactor, for example, the interior of riser 70, downcomer 50, and head 40, as discussed further hereinbelow. Introducing CO-saturated fluid into the riser of the reactor may comprise injecting CO-saturated fluid to at least one location within the riser via at least one high pressure pump and at least one injection nozzle or sprayer. Introducing CO-saturated fluid into the riser of the reactor may comprise injecting CO-saturated fluid to a plurality of locations within the riser via a plurality of high pressure pumps and a plurality of injection nozzles or sprayers.

[00122] As indicated in Figure 5, retention chamber outlet line(s) 84 may be connected to inlet nozzles 2 along the walls of riser 70 (or fast-flow zone) of reactor 30. Line(s) 84 may be utilized to introduce CO-saturated fluid to one or more pumps 1 which are operable to forcibly inject the CO-saturated fluid into reactor 30 via one or more injection nozzles 2. For example, in the embodiment of Figure 5, line 84 is connected to seven pumps, 1a-1g. Pumps 1a-1g are configured to pump the CO-saturated fluid into riser 70 of reactor 30 via seven injection nozzles or sprayers 2a-2g respectively.

[00123] A controller may be utilized to regulate the injection via each of any number of pumps and nozzles or sprayers. The one or more pumps of associated with reactor 30 may be in electronic communication with a controller for regulating the injection characteristics of each injection nozzle or sprayer 2 or the flow rate provided by venturi pump 1h. Variable frequency drives may be utilized to control each of pumps 1.

[00124] Injection may be effected via nozzles. The nozzles may be any nozzle known in the art. In applications, suitable nozzles, e.g., nozzles 1a-1g, (and cleaning nozzles 1i-1k, and 1m which will be discussed further hereinbelow) are high pressure Toftejorg rotary jet heads, available from Alfa Laval (Lund, Sweden). The flow of fluid through the nozzles causes a geared rotation around the vertical and horizontal axes. Sprayers 2 may comprise four changeable nozzles which can rotate in the vertical and horizontal directions simultaneously. Sprayers 2 may be constructed of any suitable material in any suitable form and size.

[00125] Utilization of a plurality of injection nozzles/sprayers 2 and associated pumps 1 allows injection of differing volumes and/or concentrations of fermentation feed gas into the various nozzles. In such embodiments, line 84 may be split into a plurality of lines (not shown in the embodiment of Figure 5) such that CO-saturated fluid exiting retention chamber 80 via retention chamber outlet line 84 may be introduced at various flow rates and varying concentrations into riser 70. For example, different amounts of gaseous diluent or saturated fluid may be introduced into each or some of the nozzles 2. For example, as toxicity of

microorganisms to CO_2 may be greater at greater depths (pressures), fluid injected into a lower nozzle, such as nozzle 2g, may be of a greater bacterial concentration and/or a reduced CO or CO_2 concentration as compared with fluid injected to a nozzle positioned closer to ground level G, e.g., nozzle 2a.

[00126] Introduction of CO-saturated fluid into the riser is performed such that suspension within the deep shaft reactor circulates about the divider flowing with a first linear velocity up the riser, passing over the top of the divider, and flowing with a second linear velocity down the downcomer, wherein the first linear velocity is greater than the second linear velocity.

[00127] Reactor 30 is configured such that, during operation, suspension may be circulated repeatedly between downcomer 50 ("downflow chamber"), which comprises CO-depleted suspension 50, and riser 70 ("upflow chamber"), which comprises fast flowing, CO-rich suspension. Referring still to Figure 5, reactor 30 is configured to drive the suspension through the circulating system by injection of CO-saturated fluid only into the rapid flow zone of riser 70. The undissolved gas, including primarily unconverted CO, and evolved H_2 and CO_2, in fast-flow zone 70 provides gas "lift" to drive circulation of the suspension from fast-flow zone 70 towards head 40. The theory of operation is that the suspension in downcomer 50 (*i.e.*, the slow-flow zone) has a higher density than the liquid-bubble mixture in riser 70 (*i.e.*, fast-flow zone 70). This density differential also promotes circulation from riser 70 to downcomer 50. As the circulating suspension and product gases (including hydrogen and CO_2) ascend in riser 70 (fast-flow zone) to regions of lower hydrostatic pressure (*e.g.*, the upper end of riser 70 and annular liquid region 48) the dissolved off-gas separates as bubbles. When the liquid/bubble mixture from fast-flow zone 70 enters the annular region 48 of reactor head 40, gas disengagement occurs. The disengaged gas accumulates in headspace 44 of reactor head 40 until withdrawn.

IID. Removing Fermentation Product Gas Comprising Hydrogen from the Reactor

[00128] Biologically converting CO from synthesis gas to fermentation product gas comprising hydrogen (II) further comprises (IID) removing fermentation product gas comprising hydrogen from the reactor. Fermentation product gas comprising hydrogen may be removed from the reactor by vacuum degasifying the product gas comprising hydrogen from the headspace 44, whereby suspension circulating from the top of the divider down into the downcomer becomes CO-depleted.

[00129] During operation, a headspace 44 is maintained above suspension level 43. Operation of reactor 30 may be monitored as known in the art (flow meters, PLC, etc.) such

that a headspace 44 of a desired volume exists within reactor 30. Headspace 44 may be a volume approximately 5% to about 20% of the operating suspension reactor volume. Headspace 44 is configured as a vacuum degasifier which allows/promotes gases produced/disengaged from the suspension to be removed from reactor 30, as will be discussed further hereinbelow. Vacuum degasification is utilized to promote disengagement and removal of fermentation product gas comprising hydrogen from the suspension in annular region 48 prior to reentry of the suspension into slow-flow zone 50. Headspace 44 is coupled to spillover region 16a and H_2 recovery subsystem 110.

Rapid removal of the gasification product gas from the suspension deters potential toxic effects of the gases on the microorganisms, and reduces the propensity of undesirable side reaction. Evolved gases may be collected and extracted from reactor 30 via vacuum degasification. Such vacuum may be applicable to the suspension as the suspension circulates through the lower portion (or annular liquid region 48) of reactor head 40, for example via vacuum 1n.

[00130] Biologically converting CO from synthesis gas to fermentation product gas comprising hydrogen (II) may further comprise determining the concentration of carbon monoxide in the fermentation product gas extracted from headspace 44 via fermentation product gas outlet line 88. In many applications, the selected microorganism(s) are relatively insensitive to CO concentration in the suspension. Therefore, the CO concentration in the fermentation product gas may be adjusted such that substantially all CO is consumed. Thus, system 10a may further comprise a control system in conjunction with measurement apparatus whereby the composition of the fermentation feed gas comprising CO in line 102 may be adjusted so that substantially all CO in the fermentation feed gas is consumed in reactor 30. The concentration of carbon monoxide in the fermentation feed gas (in line 102) may be reduced, the volume of fermentation feed gas reduced, or the concentration of biomass in the slurry increased if the measured amount of CO in the fermentation product gas is too high and alternatively, the concentration of the CO in the fermentation feed gas (fed via line 102) may be increased if the bacterial concentration is capable of converting a greater amount of CO to hydrogen. Thus, in embodiments, biologically converting CO from synthesis gas to fermentation product gas comprising hydrogen (II) further comprises measuring the concentration of CO in the fermentation product gas comprising hydrogen and adjusting the volume of fermentation feed gas introduced into the reactor, the concentration of carbon monoxide in the fermentation feed gas introduced into the reactor, the level of TDS in the suspension in the reactor, or a combination thereof such that the concentration of CO in

the fermentation product gas is maintained below a desired value. The desired value may be substantially zero.

[00131] A portion of the product hydrogen extracted via vacuum degasification (e.g., in fermentation gas product outlet line 88) or upgraded hydrogen (e.g., in hydrogen PSA outlet line 113) may be recycled to reactor 30 (e.g., via introduction into retention chamber 80 or inlet line 102) should the measured CO in the fermentation product gas be undesirably high. Such recycle may provide dilution while maintaining desired gas lift potential. Thus, in embodiments, adjusting the concentration of CO in the fermentation feed gas comprises combining at least a portion of the fermentation product gas with the fermentation feed gas as diluent. Operational parameters may be monitored via an operating room and touch screens, as known in the art.

[00132] Production of hydrogen via Eq. (1) involves concomitant production of equimolar amounts of carbon dioxide acid gas, which may lead to decreased pH, affecting microbial toxicity limitations with respect to CO_2, H_2 or CO. Thus, conversion of fermentation feed gas comprising CO (II) may further comprise determining the pH of suspension within the reactor, and introducing base into the reactor (e.g., via line 41d) to encourage formation of bicarbonate/pH elevation. The bicarbonate remains in the liquid phase avoiding transfer of carbon dioxide to fermentation product gas. In some applications, the pH is controlled with NaOH injection to maintain the pH of the suspension within a desired pH range by promoting conversion of excess CO_2 to soluble bicarbonate. Such a desired pH range may be from about 7.5 to about 9.5. Thus, in embodiments, biologically converting CO into fermentation product gas comprising hydrogen (II) further comprises adjusting the pH of the suspension to a pH of greater than about pH 9, such that carbon dioxide is converted to soluble bicarbonate. In some applications, pH is controlled to about pH 9 by injection of aliquots of a NaOH solution into reactor head 40. Soluble bicarbonate may be removed via a biomass separation unit 90 (discussed further hereinbelow), for example, via water dilution. In applications, the bicarbonate may be removed via precipitation from the aqueous phase.

Temperature Control System

[00133] In embodiments, biological conversion (II) further comprises controlling the temperature within the fermentation reactor. The temperature may be controlled with a temperature control system may comprising a temperature control unit in thermal communication with reactor 30 and retention chamber 80. A cooling sleeve (or "temperature-control sleeve) may be utilized to control the temperature within the reactor.

For example, reactor 30 may be surrounded by and spaced an axial distance from by a vessel having the same general shape thereof. For example, in instances where reactor 30 is cylindrical, reactor 30 may be surrounded by and separated an axial distance from a concentric cylinder. As indicated in Figure 5, reactor 30 may be surrounded by vessel 36 and separated therefrom by a distance L6. Concentric (or similarly-shaped) vessel 36 be itself surrounded by insulation, e.g. polyurethane, which separates it from the earth of the borehole. As depicted in Figure 5, temperature control fluid may be introduced the region between concentric vessel 36 and the outer sides of reactor walls 33 of reactor 30 via a line 4a. Spent temperature control fluid may be removed from the temperature control region 11 between concentric vessel 36 and the outer sides of reactor walls 33 of reactor 30 via a line 4b. Baffles may be positioned within temperature control region 11 to direct the flow of cooling fluid from the top of reactor 30 along one side to the bottom, along the bottom, and back up the opposite side of reactor 30 and out. Baffles may be welded to outer sides of reactor walls 33 and inner side of the concentric vessel 36. Temperature control region 11 and cooling sleeve or concentric vessel 36 may also be used to sterilize deep shaft reactor 30 via steam cleaning.

[00134] In embodiments in which biological conversion does not produce significant amounts of heat, cooling of reactor 30 may not be necessary. Temperature control may be desirable, however, in applications in which the ground temperature is very cold, in which applications the temperature of the suspension within reactor 30 may be maintained within a desirable or optimum range for bacterial conversion of carbon monoxide. In other instances, temperature control may be utilized for cooling the equipment when steam is used during cleaning operations. Cooling may also be desirable when the bacteria produce a significant amount of heat, in which case the temperature control system may be used to reduce the temperature of the suspension within reactor 30 to a desired or optimum level for bacterial fermentation of carbon monoxide and production of CO therefrom.

Cleaning System

[00135] Biological conversion (II) may further comprise periodically cleaning in place, or CIP. Nozzles configured for injection of CO-saturated fluid into riser 70 may be utilized for cleaning in place, or CIP. Additional spray nozzles may be positioned along the slow-flow or downcomer wide of reactor 30, as indicated in Figure 5. For example, nozzles 2i, 2j, and 2k along with associated high pressure pumps 1i, 1j, and 1k may be fluidly connected with cleaning chemicals via lines 3a and 3c, for example. Should reactor 30 comprise suspension annular region 48, an additional nozzle 2m and associated high pressure pump 1m

may be positioned along the vertical perimeter of annular suspension region 48, as indicated in Figure 5. Pump 1m and spray nozzle 2m may be fluidly connected with cleaning chemicals via, for example, cleaning lines 3a and 3b.

[00136] As mentioned hereinabove, the nozzles may be Toftejorg rotating spray devices, available from Alfa Laval (Lund, Sweden). The flow of the fluid (in this application, cleaning fluid or steam) causes the nozzles to make a geared rotation around the vertical and horizontal axes. In the first cycle, the nozzles lay out a coarse pattern on the surface of the vessel being cleaned. Subsequent cycles gradually make the pattern denser until substantially complete coverage is obtained. The jets provide a combination of physical impact and a cascade cleaning solution flow that reaches substantially all of the surfaces in the compartment being cleaned. Toftejorg nozzles are auto-cleaning by directing the cleaning media through the rotating bearing track and onto the neck of the elongated head.

[00137] Cleaning chemicals may be introduced into riser 70 via cleaning chemical lines 3a and 3d. Cleaning chemicals may be introduced into venturi 85 via line 3d such that the interior of retention chamber 80 is exposed to cleaning solution prior to introduction of the cleaning chemicals to reactor 30 via pumps 1a-1g and nozzles 2a-2g. Alternatively, cleaning chemicals may be introduced directly into each pump along riser 70 or may be introduced into retention chamber outlet line 84. Although not indicated in the embodiment of Figure 5, conservation of cleaning chemicals may be provided by a cleaning chemical recycle loop and cleaning chemical purification apparatus. Cleaning chemicals extracted from the bottom of reactor 30 may be cleaned (e.g., filtered) by the purification apparatus and recycled via the recycle loop for reuse as cleanser. For example, in applications, cleaning chemical purification apparatus may comprise a plate and frame membrane module for (continuous, semi-continuous, or periodic) removal of contaminants from spent cleaning solution prior to reinjection into reactor 30 or retention chamber 80. In such a manner, the cleaning system continuously operated via cleaning chemical recirculation. This recycle/reuse of cleaning chemical(s) may reduce the amount of water and/or cleaning chemical(s) utilized during cleaning operations.

[00138] The cleaning chemicals may comprise any suitable cleaning solution and may be, for example, hydrophilic, oleophilic, amphiphilic. The cleaning solution is supplied to the feed streams utilizing at least one vessel with necessary components, such as tubes, pipes, and pumps. Cleaning chemicals may comprise, for example, caustic soda, chlorine solution, biocide solution, or steam. The composition of the cleaning solution may be varied during a cleaning cycle, depending on the objectives of cleaning needed and the surface to be cleaned.

In embodiments, the cleaning solution is heated or cooled prior to being introduced into cleaning nozzles/sprayers 2. Although temperature control may not be needed during regular fermentation, temperature control may be desirable during cleaning operations, e.g., using steam cleaning. In embodiments, a cleaning cycle comprises emptying the vessels to be cleaned, optionally rinsing with water, injecting cleaning chemicals, optional rinsing, and finally injecting steam.

Utilization of Serial Reactors

[00139] In applications (not depicted in Figure 5), biologically converting CO produced via gasification into hydrogen (II) comprises utilization of a plurality of reactors arranged in series. In such arrangements, a first reactor R1 may be fed a feed gas having a CO concentration [X1], may comprise a suspension having a microorganism concentration [M1], and may have a vertical depth D1; a second reactor R2 of the series may be fed a fermentation feed gas (gas exiting first reactor R1) having a CO concentration [X2], may comprise a suspension having a microorganism concentration [M2], and may have a vertical depth D2; a third reactor R3 of the series may be fed a feed gas (gas exiting second reactor R2) having a CO concentration [X3], may comprise a suspension having a microorganism concentration [M3], and may have a vertical depth D3; and so on. High CO (and/or other gas, e.g., CO_2) concentration may be toxic to the microorganisms. Thus, lower pressure (reduced depth and thus reduced toxicity) may be desired when [CO] in the fermentation feed gas is higher. As the fermentation feed gas fed into subsequent reactors in serial application is lower, subsequent reactors in the series may have deeper depths, D. Furthermore, as the CO concentration, [X] of the fermentation feed gas to subsequent serial reactors is reduced, the subsequent reactors may convert substantially all of the carbon monoxide to hydrogen while operating with a lower microorganism concentration, [M]. Therefore, in applications a plurality of deep shaft reactors aligned in series are utilized for biological conversion and [X1]>[X2]>[X3], and so on. In applications, a plurality of deep shaft reactors aligned in series are utilized for biological conversion and D1<D2<D3, and so on. In applications, a plurality of deep shaft reactors aligned in series are utilized for biological conversion and [M1]>[M2]>[M3], and so on. In applications, a plurality of deep shaft reactors aligned in series are utilized for biological conversion and [X1]>[X2]>[X3]... ; D1<D2<D3...; and [M1]>[M2]>[M3]. In this manner, the pressure of operation, the concentration of biomass within each of a plurality of reactors, and/or the CO content of the feed gas to each of a plurality of reactors may be modified (i.e., the depth varied) to provide optimum conditions for bacterial fermentation. Utilization of a plurality of deep shaft reactors in series with

various inlet concentrations of CO in the fermentation feed gas and/or various depths allow manipulation of the optimum operating conditions (toxicity points) of the bacteria. Such serial operation may provide flexibility in operation when feed materials gasified to produce synthesis gas varies, changing the fermentation feed gas obtained therefrom.

III. Converting Hydrogen in Fermentation Product Gas to Useful Product

[00140] WTE method 10 further comprises: (III) converting at least a portion of the hydrogen in the fermentation product gas to useful product. Such useful product may be electricity, proceeds, upgraded hydrocarbon fuels, desirable chemical compounds or a combination thereof.

IIIA/B. Removing Non-Hydrogen Components from Fermentation Product Gas/Producing Electricity via Hydrogen Fuel

[00141] Converting at least a portion of the hydrogen in the fermentation product gas to useful product (III) may comprise (IIIA) removing non-hydrogen components from the fermentation product gas comprising hydrogen, to increase the purity of the hydrogen product and (IIIB) combusting or electro-chemically converting hydrogen in fermentation product gas to electricity.

[00142] Converting at least a portion of the hydrogen in the fermentation product gas to useful product may comprise utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel. Utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel may further comprise at least one selected from the group consisting of increasing the purity of the hydrogen in the fermentation feed gas via one or more hydrogen pressure swing adsorption units, combusting at least a portion of the fermentation product gas, and electrochemically converting at least a portion of the hydrogen to electricity.

[00143] The disclosed WTE method 10 may be utilized to produce fermentation product gas comprising at least 90% hydrogen, at least about 99% hydrogen, at least about 99.9% hydrogen, or at least about 99.99% hydrogen. The fermentation product gas may comprise ultra-pure hydrogen. Given enough time, for example, or using serial reactors 30, fermentation product gas extracted via fermentation product outlet line 88 may comprise little or substantially no CO.

[00144] Fermentation product gas (e.g., extracted via fermentation product gas outlet line 88) may be introduced into a hydrogen recovery/utilization subsection 110. If fermentation product gas comprising hydrogen comprises about 99% hydrogen, fermentation product gas may be introduced, as in the embodiment of Figure 8a, via pump 1n into gas

generator set 111. Additional fuel may be introduced into Gas Generator (GasGen) set 111 via additional fuel line 118. Additional fuel may be introduced upstream of GasGen set 111 or may be introduced directly into GasGen Set 111. The additional fuel may be any fuel, for example, methane. Alternatively, if the hydrogen in the fermentation product gas is less than about 99% pure, further clean-up (not shown in the embodiment of Figure 8a) may be performed upstream of GasGen set 111. GasGen set 111 is any suitable gas generator capable of converting hydrogen to electricity, which is represented in Figure 8a as line 95b.

[00145] If fermentation product gas comprising hydrogen comprises about 99% hydrogen, fermentation product gas may be introduced, as in the embodiment of Figure 8b, via pump 1n into purification unit 112. In this embodiment, fermentation product gas comprising hydrogen is introduced into purification unit 112, wherein non-hydrogen components are removed from the fermentation product gas. Removal of non-hydrogen components may be performed via any means known in the art, for example, hydrogen pressure swing adsorption. Thus, in embodiments, purification unit 112 is a hydrogen PSA unit. Exhaust gas separated from the fermentation product gas within PSA 112 PSA may exit purification unit 112 via exhaust gas line 96. Depending on CO_2 and nitrogen compound levels within the exhaust gas, the exhaust gas may be vented to the atmosphere via a chimney (not shown in Figure 8b). High purity hydrogen gas removed from PSA 112 may be introduced (e.g., via a PSA outlet line 113 into, for example, a fuel cell. In embodiments, PSA 112 is capable of producing high purity hydrogen comprising at least 99% hydrogen by weight; alternatively greater than 99.9% hydrogen by weight; alternatively greater than 99.99% hydrogen by weight. Fuel cell 114 may be one or more high or low temperature fuel cells suitable for producing electricity using hydrogen as fuel. For example, fuel cell(s) 114 may be selected from proton exchange membrane fuel cells or PEMs, molten carbonate fuel cells or MCFCs, and solid oxide fuel cells or SOFCs. In embodiments, oxygen produced in oxygen-enrichment unit 166 (when oxygen enrichment unit 166 comprises an ASU) is also introduced via oxygen inlet line 180b into fuel cell 114 for use as oxidant. Electricity is produced within fuel cell 114 from the hydrogen within the fermentation product gas, as indicated by outlet line 95c. In general, the higher the temperature, the lower the constraints on fuel mixtures that are suitable for fuel cell(s) 114. Low and intermediate temperature operation fuel cells, e.g. PEM fuel cells, may require very low concentrations of CO, e.g. [CO] < 10ppm. Higher temperature fuel cell(s) 114 may have less stringent fuel requirements.

[00146] As with the electricity 95a generated in steam turbine 218, electricity 95b/95c generated in hydrogen recovery subsystem 110 may be used throughout WTE system 10a, for example, for running oxygen-enhancement unit 166 and/or hydrogen upgrading unit 112, or may be utilized in another associated part of system 10a or sold for profit.

[00147] Alternatively, fermentation product gas comprising hydrogen or high purity hydrogen in PSA outlet line 113 may be utilized for a purpose other than electricity generation. For example, the hydrogen may be utilized for chemical production, hydrocarbon product upgrading, may be sold for a profit, or other uses.

[00148] Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The embodiments described herein are to be construed as illustrative and not as constraining the remainder of the disclosure in any way whatsoever. While the preferred embodiments of the invention have been shown and described, many variations and modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims, including all equivalents of the subject matter of the claims. The disclosures of all patents, patent applications and publications cited herein are hereby incorporated herein by reference, to the extent that they provide procedural or other details consistent with and supplementary to those set forth herein.

References:

Maness, Pin-Ching, Jie Huang, Sharon Smolinski, Vekalet Tek, and Gary Vanzin, "Energy generation from the CO oxidation-hydrogen production pathway in *Rubrivivax gelatinosus*," June 2005 *Applied and Environ. Microbiol.* 71:2870-2874.

Merida, Walter, Pin-Ching Maness, Robert C. Brown and David B. Levin, "Enhanced hydrogen production from indirectly heated, gasified biomass, and removal of carbon gas emissions using a novel biological gas reformer," 2004 *Int. J. Hydrogen Energy* 29:283-290.

Maness, Pin-Ching, Sharon Smolinski, Anne C. Dillon, Michael J. Heven, and Paul F. Weaver, "Characterization of the oxygen tolerance of a hydrogenase linked to a carbon monoxide oxidation pathway in *Rubrivivax gelatinosus*," June 2002 68:2633-2636.

Maness, Pin-Ching and Paul F. Weaver, "Hydrogen production from a carbon-monoxide oxidation pathway in *Rubrivivax gelatinosus*," 2002 *Int. J. Hydrogen Energy* 27:1707-1411.

CLAIMS

What is claimed is:

1. A waste to energy method comprising:

gasifying a feed material comprising waste, to produce gasifier gaseous product comprising synthesis gas and a gasifier non-gaseous product, wherein gasifying is performed at a gasification temperature and a gasification pressure;

biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen, wherein at least a portion of the carbon monoxide is obtained from the gasifier gaseous product; and

utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel.

2. The method of claim 1 wherein biologically converting comprises introducing a fermentation feed gas into a deep shaft reactor, wherein the deep shaft reactor contains a suspension comprising a liquid nutrient medium lacking a carbon source and photoactivated microorganisms capable of carrying out the water-gas shift reaction; has a vertical depth and a shaft width; comprises a downcomer and a riser separated by a divider; and comprises a headspace above a normal operating suspension fill line.

3. The method of claim 2 wherein microorganisms capable of carrying out the water-gas shift reaction are selected from the group consisting of *Rubrivivax gelatinosus*, *Rhodospirillum rubrum,* and *Rhodopseudomonas palustris*.

4. The method of claim 2 wherein biologically converting further comprises:

saturating a fluid with CO gas by contacting, under pressure, the fluid with fermentation feed gas comprising CO in a retention chamber;

introducing the saturated fluid into the riser of the deep shaft reactor such that the suspension within the deep shaft reactor circulates about the divider flowing with a first linear velocity up the riser, passing over the top of the divider, and flowing with a second linear velocity down the downcomer, wherein the first linear velocity is greater than the second linear velocity; and

vacuum degasifying a product gas comprising hydrogen from the headspace, whereby suspension circulating from the top of the divider down into the downcomer becomes CO-depleted.

5. The method of claim 4 further comprising maintaining a desired level of total dissolved solids within the deep shaft reactor by continuously, periodically or semi-

continuously removing an extracted portion of suspension from a top portion of the deep shaft reactor.

6. The method of claim 5 further comprising separating microorganisms from the extracted portion of suspension to produce a sludge comprising separated microorganisms and a biomass-reduced effluent.

7. The method of claim 6 wherein separating microorganisms from the extracted portion of suspension comprises ultrafiltration, microfiltration, centrifugation, decanting, clarification, or a combination thereof.

8. The method of claim 6 further comprising recycling at least a portion of the biomass-reduced effluent to the deep shaft reactor.

9. The method of claim 8 wherein the fluid saturated with CO comprises at least a portion of the biomass-reduced effluent.

10. The method of claim 6 further comprising gasifying at least a portion of the sludge to produce additional gasifier gaseous product comprising synthesis gas.

11. The method of claim 5 further comprising utilizing at least a portion of the extracted suspension to produce methane gas via fermentation.

12. The method of claim 5 further comprising combining at least a portion of the biomass in the extracted suspension with suitable substrates and fermenting to produce at least one selected from butanol, ethanol and acetone.

13. The method of claim 4 further comprising:

extracting a CO-depleted portion of suspension from a lower portion of the downcomer; wherein the fluid comprises at least a portion of the CO-depleted portion of suspension extracted from the lower portion of the downcomer.

14. The method of claim 4 further comprising adjusting the pH of the suspension to a pH of greater than about pH 9, such that carbon dioxide is converted to soluble bicarbonate.

15. The method of claim 4 wherein the majority of the biological conversion is performed in the absence of substantial light.

16. The method of claim 4 wherein introducing CO-saturated fluid into the riser of the deep shaft reactor comprises injecting CO-saturated fluid to at least one location within the riser via at least one high pressure pump and at least one injection nozzle or sprayer.

17. The method of claim 4 wherein introducing CO-saturated fluid into the riser of the deep shaft reactor comprises injecting CO-saturated fluid to a plurality of locations within the riser via a plurality of high pressure pumps and a plurality of injection nozzles or sprayers.

18. The method of claim 4 wherein there is no direct introduction of feed source into the downcomer of the deep shaft reactor.

19. The method of claim 4 further comprising forming a mixture comprising the fluid and the fermentation feed gas and increasing the pressure of the mixture.

20. The method of claim 2 further comprising measuring the concentration of CO in the fermentation product gas comprising hydrogen and adjusting the volume of fermentation feed gas introduced into the deep shaft reactor, the concentration of carbon monoxide in the fermentation feed gas introduced into the deep shaft reactor, the level of TDS in the deep shaft reactor, or a combination thereof such that the concentration of CO in the fermentation product gas is maintained below a desired value.

21. The method of claim 20 wherein adjusting the concentration of CO in the fermentation feed gas comprises combining at least a portion of the fermentation product gas with the fermentation feed gas as diluent.

22. The method of claim 20 wherein the desired value is substantially zero.

23. The method of claim 2 wherein the vertical depth of the deep shaft reactor is in the range of from about 50m to about 600m.

24. The method of claim 1 wherein the gasification temperature is greater than about 2200°C.

25. The method of claim 24 wherein the gasification pressure is about atmospheric pressure.

26. The method of claim 1 wherein gasifying comprises plasma gasifying.

27. The method of claim 26 wherein plasma gasifying further comprises introducing oxidant and feed material comprising waste into at least one plasma gasifier.

28. The method of claim 27 wherein the oxidant is selected from oxygen-enriched air and oxygen.

29. The method of claim 1 wherein the non-gaseous product passes EPA-mandated Toxicity Characteristic Leachate Procedure.

30. The method of claim 1 wherein the feed material comprising waste is selected from agricultural waste, forestry waste, biomass, municipal solid waste, auto shredder residue, yard waste, industrial waste, coal, bitumen, coke, and combinations thereof.

31. The method of claim 1 wherein biologically converting carbon monoxide in a fermentation feed gas to produce a fermentation product gas comprising hydrogen is performed substantially anaerobically.

32. The method of claim 1 wherein utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel further comprises increasing the purity of the hydrogen in the fermentation product gas.

33. The method of claim 1 wherein utilizing at least a portion of the fermentation product gas comprising hydrogen as fuel further comprises at least one selected from the group consisting of increasing the purity of the hydrogen in the fermentation feed gas via one or more hydrogen pressure swing adsorption units, combusting at least a portion of the fermentation product gas, and electrochemically converting at least a portion of the hydrogen to electricity.

34. The method of claim 1 further comprising extracting heat from the gasifier gaseous product comprising synthesis gas.

35. The method of claim 34 wherein extracting heat from the gasifier gaseous product further comprises using the extracted heat for preheating oxidant, generating steam, or both.

36. The method of claim 1 further comprising removing particulate from the gasifier gaseous product.

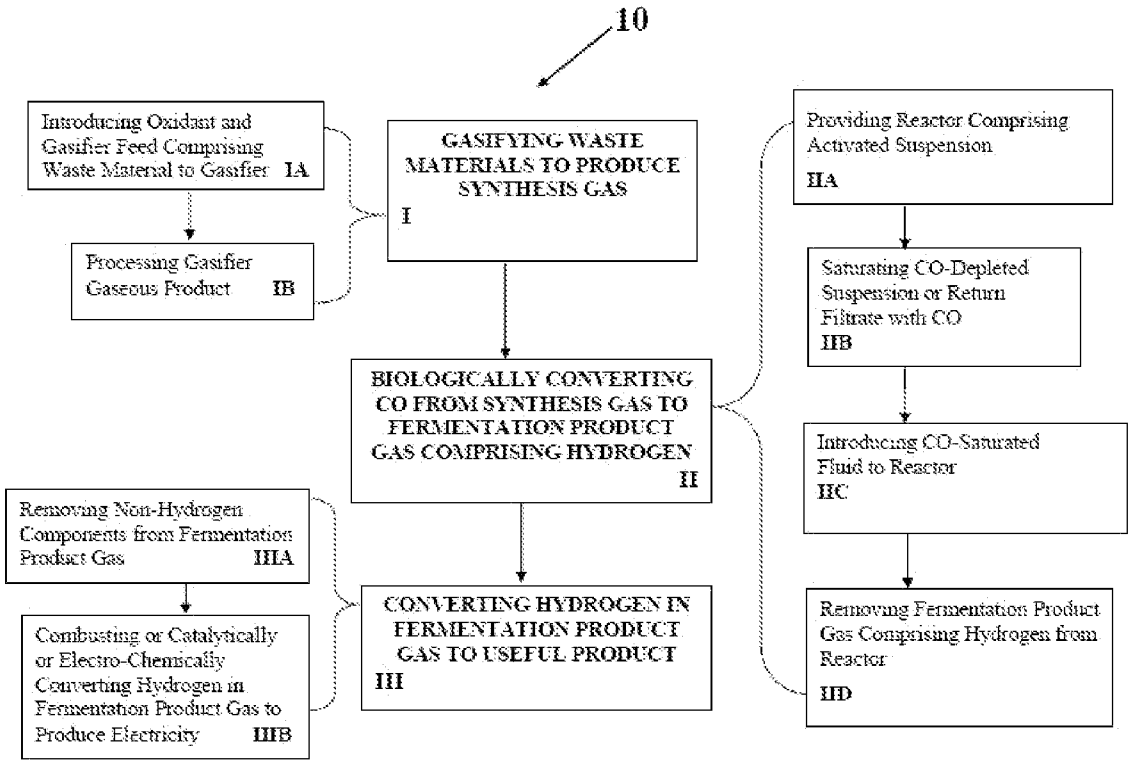
10
Introducing Oxidant and Gasifier Feed Comprising Waste Material to Gasifier IA
Processing Gasifier Gaseous Product IB
GASIFYING WASTE MATERIALS TO PRODUCE SYNTHESIS GAS I
BIOLOGICALLY CONVERTING CO FROM SYNTHESIS GAS TO FERMENTATION PRODUCT GAS COMPRISING HYDROGEN II
Removing Non-Hydrogen Components from Fermentation Product Gas IIIA
Combusting or Catalytically or Electro-Chemically Converting Hydrogen in Fermentation Product Gas to Produce Electricity IIIB
CONVERTING HYDROGEN IN FERMENTATION PRODUCT GAS TO USEFUL PRODUCT III
Providing Reactor Comprising Activated Suspension IIA
Saturating CO-Depleted Suspension or Return Filtrate with CO IIB
Introducing CO-Saturated Fluid to Reactor IIC
Removing Fermentation Product Gas Comprising Hydrogen from Reactor IID

FIG. 1

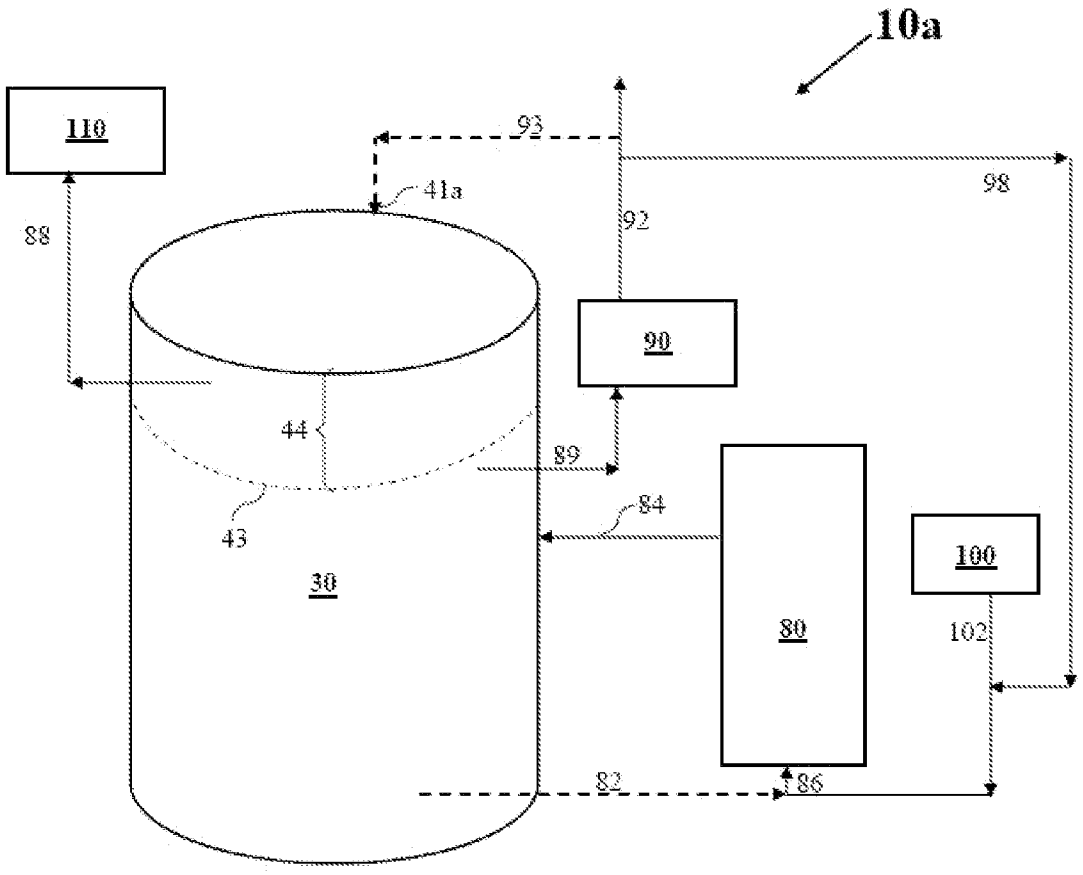

FIG. 2

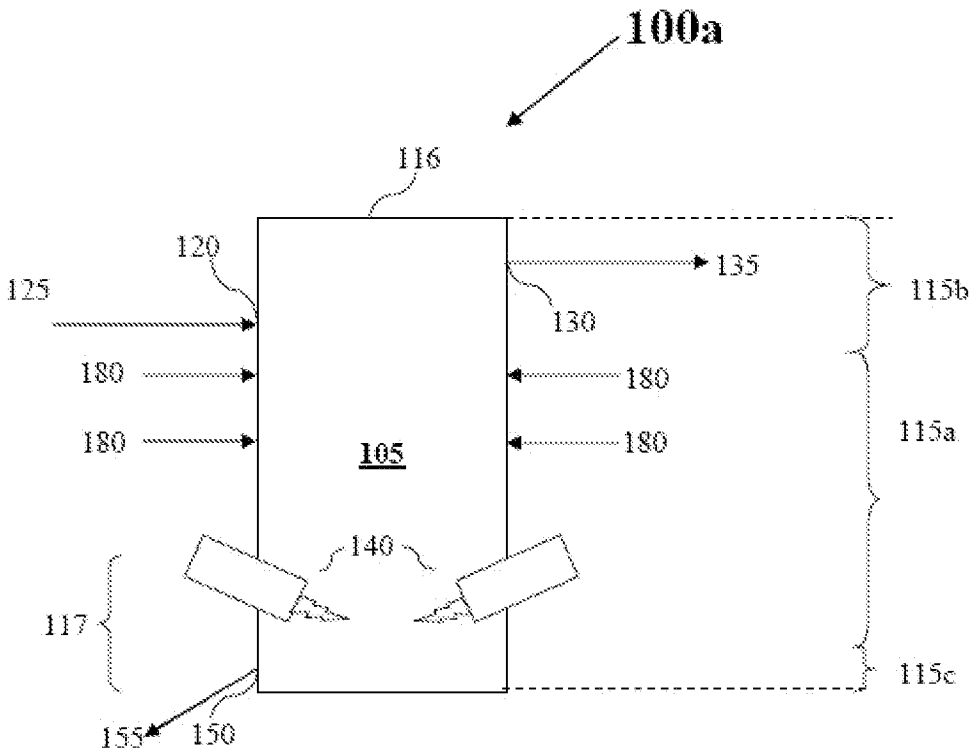
100a
116
120
125
135
130
115b
180
180
180
180
115a
105
140
117
115c
155
150

FIG. 3

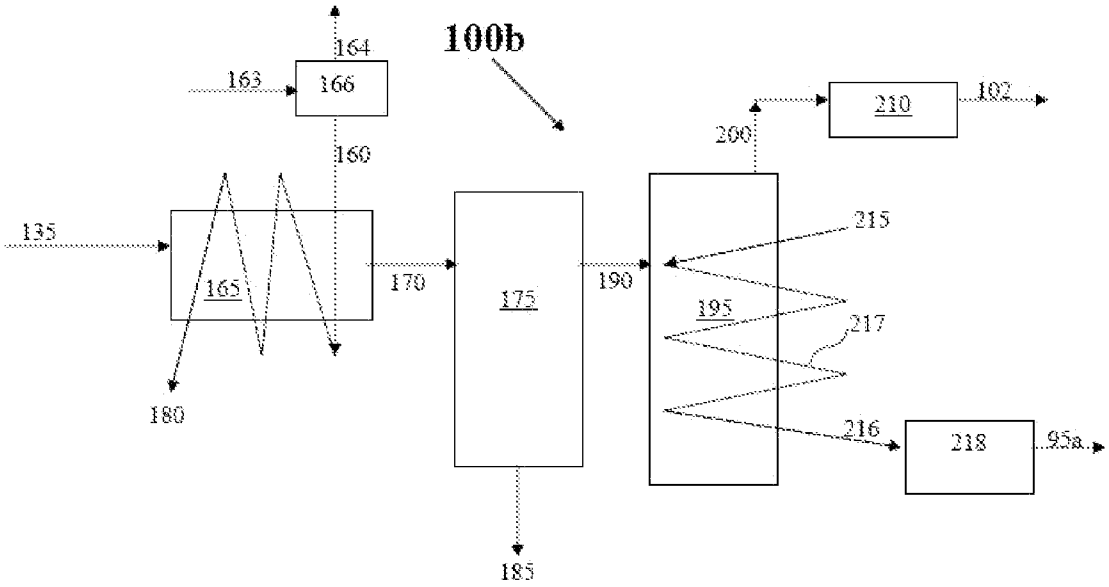
100b
164
163
166
160
135
165
170
175
190
180
185
200
210
102
215
195
217
216
218
95a

FIG. 4

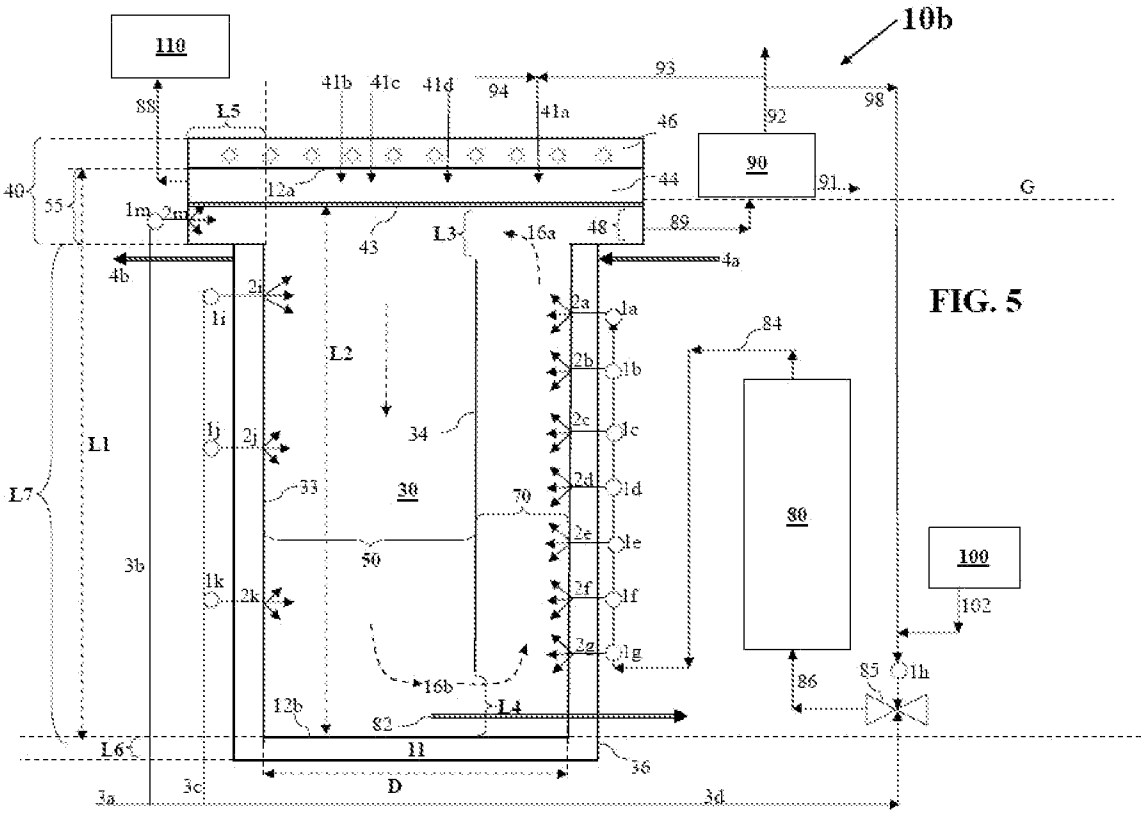
10b
110
88
L5
41b
41c
41d
94
41a
93
98
92
46
90
91
G
40
55
12a
44
1m
2m
43
L3
16a
48
89
4b
4a
2i
1i
2a
1a
84
L2
2b
1b
34
2c
1c
L1
1j
2j
2d
1d
L7
33
30
70
80
2e
1e
50
100
3b
1k
2k
2f
1f
102
2g
1g
16b
86
85
1h
12b
82
L4
L6
11
36
3a
3c
D
3d

FIG. 5

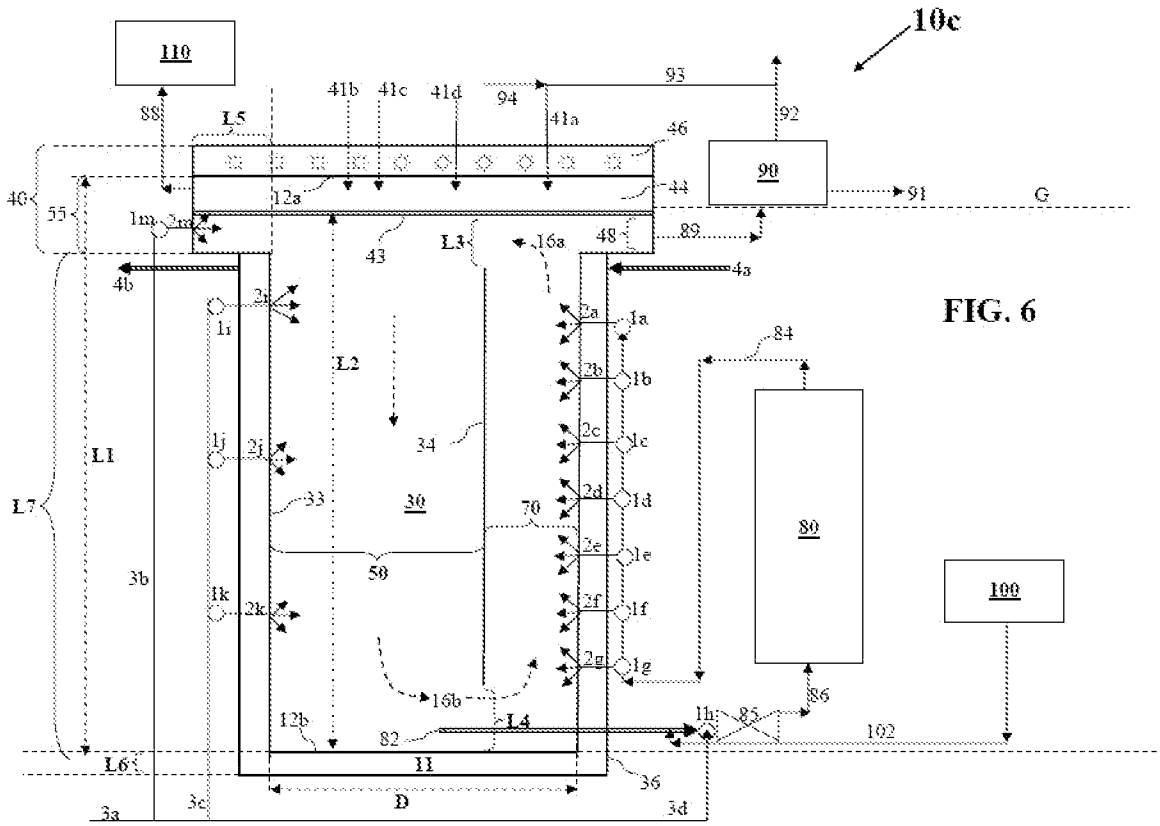
10c
110
88
L5
41b
41c
41d
94
41a
93
92
46
90
91
G
40
55
12a
44
1m
2m
43
L3
16a
48
89
4b
4a
2i
1i
2a
1a
3b
1b
2c
1c
1j
2j
34
L1
L2
2d
1d
33
30
70
84
80
L7
2e
1e
50
3b
100
1k
2k
3f
1f
2g
1g
16b
L4
86
1h
85
102
12b
82
L6
11
36
3a
3c
D
3d

FIG. 6

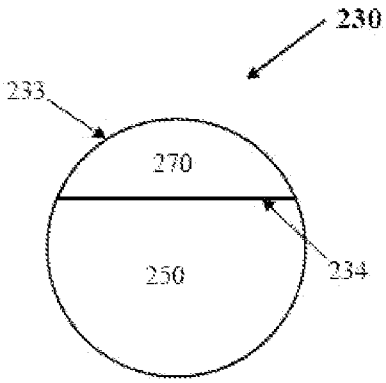

FIG. 7a

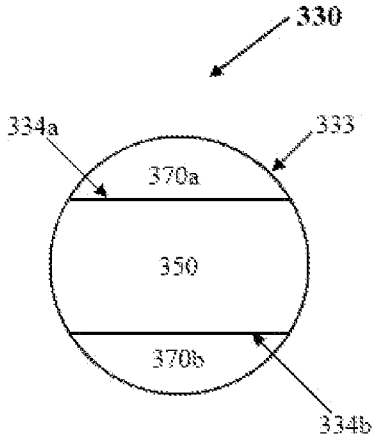

FIG. 7b

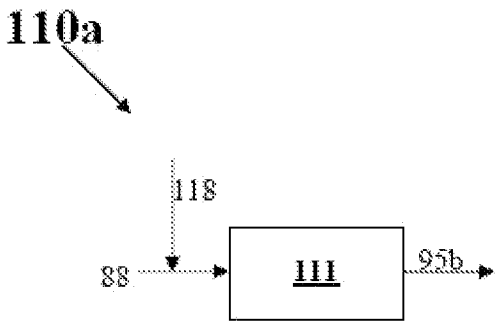

FIG. 8a

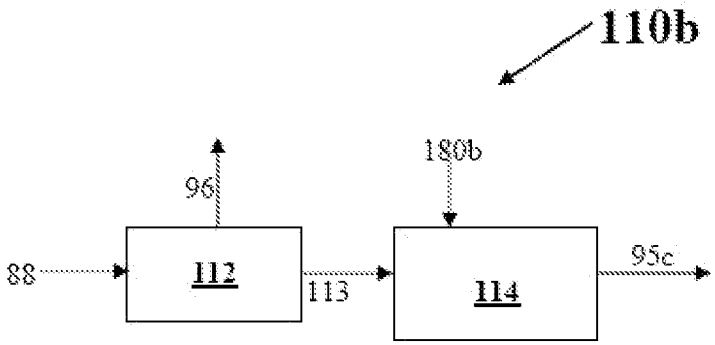

FIG. 8b