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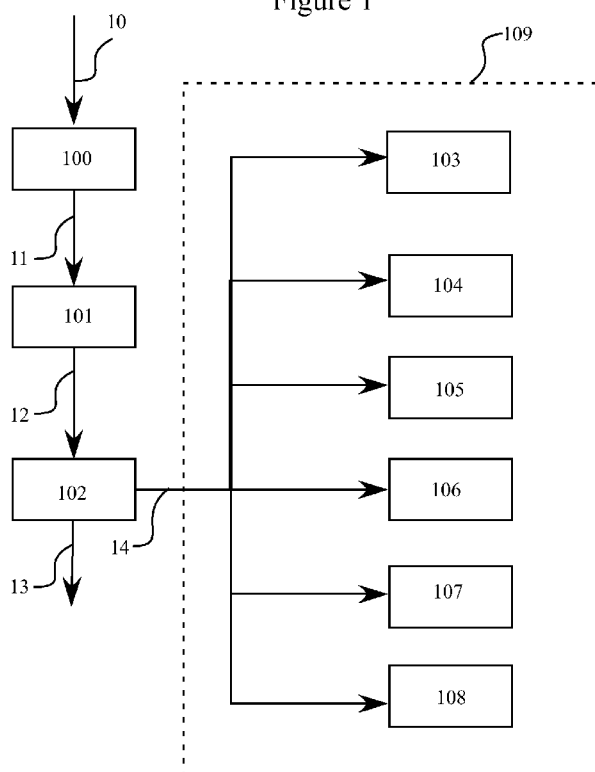
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(54) Title: INTEGRATED METHOD FOR PRODUCING A FUEL COMPONENT FROM BIOMASS AND SYSTEM THEREFOR

Figure 1



(57) Abstract: Disclosed here are integrated methods and systems for producing fuel from biomass. The methods and systems pertain to gasifying a feed derived from biomass fermentate separation residue, such as corn-based distiller's grains, and producing a liquid transportation fuel component, such as aviation turbine fuel, from the gasified feed in a hydrocarbon synthesis reactor. At least a portion of the waste heat from the hydrocarbon synthesis reactor is supplied to a thermal process for liquefying, fermenting or distilling a biomass, or to a thermal process for separating or treating a biomass fermentate separation residue.

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INTEGRATED METHOD FOR PRODUCING A FUEL COMPONENT FROM BIOMASS AND SYSTEM THEREFOR

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a non-provisional utility application claiming priority under 35 U.S.C. 119(e) of prior-filed copending provisional application serial number 60/953,364, filed 01 August 2007, entitled "Methods For Converting Biomass Into Transportation Fuel By Integrating Gasification And Fischer-Tropsch Conversion Systems Into Existing Ethanol Plants", which is hereby incorporated by reference in its entirety.

BACKGROUND

[0002] The present disclosure generally relates to integrated methods and systems for converting biomass into fuels. In particular, some embodiments herein relate to integrated methods for converting corn-based biomass into aviation jet fuel.

[0003] The United States imports over 60% of its transportation fuel. Any significant disruption overseas could result in significant deleterious effects to the current transportation capabilities and economy of the United States and elsewhere. Moreover, conventional transportation fuels have become associated with an undesirable elevation in greenhouse gas emissions, which are thought to contribute to global climate change. In an effort to address both of these unwanted situations, researchers have begun turning to alternative fuel sources, including biofuels, to replace the fossil-fuel derived products used today.

[0004] Biofuel can be broadly defined as solid, liquid, or gas fuel consisting of, or derived from, biomass. Biomass is any material derived from recently living organisms, including plants, animals and the byproducts thereof, and is a renewable energy source based on the carbon cycle. Some examples of agricultural products that can be

specifically grown for biofuel production include corn, soybeans, rapeseed, wheat and sugar cane. Biofuel is considered an important means of reducing greenhouse gas emissions, as well as increasing energy security by providing a viable alternative to currently used fossil fuels.

[0005] Currently, corn (or other biomass) can be used to manufacture ethanol, which itself is a burgeoning transportation fuel. Ethanol plants can use corn (or other biomass) to produce ethanol, but usually also produce large quantities of biomass fermentate distillation residues, such as distiller's grain, as a byproduct of the fermentation and distillation process. However, as the number of ethanol plants continues to multiply, the market for biomass fermentate distillation residues such as distiller's grain becomes increasingly saturated, resulting in a steady decline in prices and threatening an important revenue stream for ethanol plant owners.

[0006] Accordingly, there remains a need for methods for manufacturing transportation fuel that not only addresses the security and greenhouse gas issues set forth previously, but that also provides support to the ethanol industry as a fossil-fuel alternative.

BRIEF SUMMARY OF THE INVENTION

[0007] One embodiment of the present invention is directed to an integrated method for producing fuel from biomass, which method comprises the steps of: (a) providing a feed comprising biomass fermentate separation residue; (b) gasifying feed from step (a) in a gasification reactor to produce a mixture comprising CO and H₂; (c) contacting the mixture comprising CO and H₂ with a hydrocarbon synthesis catalyst in a synthesis reactor to produce heat and an effluent comprising a liquid transportation fuel component; and (d) supplying at least a portion of the heat to at least one thermal process selected from the group consisting of biomass liquefaction, fermentation, fermentation product distillation, dehydrating agent regeneration, fermentate separation residue concentrating, and fermentate separation residue drying.

[0008] A further embodiment of the present invention is directed to an integrated method for producing a turbine fuel from corn-based biomass, the method comprising the steps of: (a) providing a feed comprising corn-based biomass fermentate distillation residue; (b) gasifying feed from step (a) in a gasification reactor to produce a mixture comprising CO and H₂; (c) contacting the mixture comprising CO and H₂ with a hydrocarbon synthesis catalyst in a synthesis reactor to produce heat and an effluent comprising a liquid turbine fuel component; and (d) supplying at least a portion of the heat to at least three thermal processes selected from the group consisting of corn liquefaction, corn mash fermentation, corn fermentation product distillation, corn-based ethanol dehydrating agent regeneration, corn mash fermentate distillation residue concentrating, and corn mash fermentate distillation residue drying.

[0009] A yet further embodiment of the present invention is directed to an integrated system for producing fuel from biomass, the system comprising, (a) a unit configured to provide a feed comprising biomass fermentate separation residue; (b) a gasification reactor for gasifying feed from unit (a) to produce a mixture comprising CO and H₂; (c) catalytic hydrocarbon synthesis zone configured to react the mixture comprising CO and H₂ to produce heat and an effluent comprising a liquid transportation fuel component; and (d) at least one heat supply conduit configured to supply at least a portion of said heat to at least one thermal process selected from the group consisting of biomass liquefaction, fermentation, fermentation product distillation, dehydrating agent regeneration, fermentate separation residue concentrating, and fermentate separation residue drying.

[0010] Other features and advantages of this invention will be better appreciated from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a block flow diagram schematically setting forth methods in accordance with embodiments of the invention.

[0012] Figure 2 is an illustrative and schematic flow-chart of a method for producing corn-based distiller's grains, in accordance with embodiments of the invention.

[0013] Figure 3 is a schematic diagram of a mode of removing heat from a hydrocarbon synthesis reactor, in accordance with embodiments of the invention.

[0014] Figure 4 is a block flow diagram, schematically setting forth variant methods in accordance with other embodiments of the invention.

DETAILED DESCRIPTION

[0015] As noted, an embodiment of the present invention is directed to an integrated method and system for producing fuel from biomass. In particular, the method and systems described herein enable the efficient and effective utilization of waste heat from hydrocarbon synthesis of liquid transportation fuel components, in various thermal processes.

[0016] Referring now to Figure 1, is shown a block flow diagram, schematically setting forth methods in accordance with embodiments of the invention. A biomass fermentate separation residue 10 is supplied to a step of providing 100 a feed comprising the biomass fermentate separation residue 10. As will be described in more detail later in this disclosure, the step of "providing" 100 may comprise a pretreatment step such as pyrolysis, catalytic conversion, drying, concentrating, and/or charring (not specifically shown here). Provided feed 11 comprising biomass fermentate separation residue is recovered from providing step 100. The provided feed 11 is then supplied to a gasifying step 101 in a gasification reactor, to produce a mixture 12 comprising CO and H₂. This mixture 12 may be supplied (either directly or indirectly) to a contacting step 102 wherein the mixture 12 is contacted with a hydrocarbon synthesis catalyst in a synthesis reactor to produce heat 14 and an effluent 13 comprising a liquid transportation fuel component.

[0017] Heat 14 may be supplied to any one or more of six thermal processes 109, shown collectively in a dotted box. The six thermal processes are biomass liquefaction

103, fermentation 104, fermentation product distillation 105, dehydrating agent regeneration 106, fermentate separation residue concentrating 107, and fermentate separation residue drying 108.

[0018] As used herein, the term "biomass" is broadly defined as generally including materials derived from plants, such as woody materials, forest residues, agricultural residues, or crops; or the like. Thus, the biomass as used herein includes materials that are formed as a result of photosynthesis. This is significant for the production of liquid transportation fuel components that are to be considered "carbon-neutral" or even "carbon-negative", in the context of carbon-containing fuels as suspected climate-change agents.

[0019] The woody materials and forest residues may include wood, woodchips, saw dust, bark or other such products from trees, straw, grass, and the like. Agricultural residue and crops may further include short rotation herbaceous species, husks such as rice husk, coffee husk, etc., maize (i.e., corn), wheat, corn stover, oilseeds, residues of oilseed extraction, other grains, and the like. The oilseeds may be typical oil bearing seeds like soybean, camolina, canola, rapeseed, corn, cottonseed, sunflower, safflower, olive, peanut, and the like. Biomass may also include material obtained from agro-processing industries such as the oil industry, e.g., a deoiled residue after extraction of oil from the oil seeds. Biomass may also include other tree-based products such as shells, e.g., coconut shell, almond shell, walnut shell, sunflower shell, and the like. Cellulosic fibers like coconut, jute, and the like, may also constitute all or part of biomass. The biomass may also include algae, microalgae, and the like. It could also include agro-products after preliminary processing. As an example, this might include feedstocks such as bagasse (obtained after juice removal from sugarcane), cotton gin trash, and the like.

[0020] Methods in accordance with embodiments comprise a step of providing a feed comprising biomass fermentate separation residue. Such residues can be those produced as a by-product of the separation (e.g., distillation) of biomass fermentation into components. The biomass which is fermented is typically one or more plant biomass selected from woody materials, forest residues, agricultural residues, crops; and the like.

Typically, biomass can be fermented microbially to produce chemicals such as alcohols and other organic chemicals. Fermentation-derived alcohols can include butanol and ethanol, and other (usually volatile) organic chemicals can include ketones, carboxylic acids, aldehydes, and the like. These chemicals are desirable products of the biomass fermentation process, but must be separated out from the fermentate. In general, a typical method of separating a desirable volatile product such as ethanol from a biomass fermentate can involve the distillation of the fermentate. However, other separation methods such as pervaporation or membrane separation can also be employed to recover the desired volatile organic product from the fermentate. The portion which is rejected from the separation process when is the "biomass fermentate separation residue"; it is this latter material which is employed in methods according to embodiments of the invention.

[0021] Fermentation processes in accordance with embodiments of the present invention usually involve microbial (e.g., yeast-mediated or bacterial) conversion of a biomass-derived feedstock. In one illustrative (but non-limiting) embodiment, corn can be fermented to produce a fermentate comprising ethanol. In a typical ethanol production process utilizing corn as the feedstock, the corn may be firstly ground to produce a milled corn. The milling can be either dry milling or wet milling. The meal can then be mixed with water and an enzyme, such as alpha-amylase, and then passed to cookers to liquefy starch into a mash. Heat may then be applied at this stage to enhance liquefaction. In some embodiments, cooking to a temperature as high as 150°C may be employed. In some further typical embodiments, the mash from the cookers may be cooled and a secondary enzyme, such as glucoamylase, can be added to convert the liquefied starch to fermentable sugars. Yeast can then be added to the mash to ferment the sugars to ethanol and carbon dioxide. One or more fermenters can be used.

[0022] The fermented mash, now called beer, generally contains about 10% ethanol but additionally may contain non-fermentable solids from the corn and yeast cells. Fermented mash can then be transferred to a distillation system to remove ethanol from the solids and the water. The alcohol is typically collected from the distillation system at azeotropic (usually about 95%) concentration, and the distillation residue (sometimes

called stillage) is also collected. Once distillation residue is dried and/or concentrated, it is then termed distiller's grain. As noted, one exemplary embodiment of a biomass fermentate separation residue is distiller's grain.

[0023] Referring now to Figure 2, here is shown an illustrative and schematic flow-chart of a method for producing one form of biomass fermentate separation residue, namely, corn-based distiller's grains. Corn is supplied through 15 and is fine milled in 200 to expose its starch. Milled corn is supplied through 16 to cooker 201, to which is added enzymes (not specifically shown) and heat via steam line 17. Cooker 201 is an example of a thermal process which may employ heat recovered from the hydrocarbon synthesis reactor. Cooked corn is sent through line 18 to fermenter 202, to which is also supplied yeast through 19 and enzymes through 20. The fermented corn mash ("fermentate") is supplied via 21 to distillation apparatus 203. Steam is supplied through 22 to drive distillation of the corn mash. From the overhead of distillation apparatus 203 is collected azeotropic ethanol through 23. This azeotropic ethanol is then passed to an active bed 205 of dehydrating agent, to produce substantially anhydrous ethanol via 27. A spent bed 206 of dehydrating agent, which is offline from dehydrating duty, is regenerated by passage of an optionally heated inert gas through 28, to drive off water in 29.

[0024] From the bottoms of distillation apparatus 203 is collected corn-based stillage, which is sent via line 24 to a processor 204, wherein the stillage is processed through a centrifuge and heated dryer to remove liquids. Heat is indirectly supplied through line 25 (in the form of hot gas) and dried distiller's grains are collected via line 26.

[0025] There are various grades of distiller's grains recovered as corn-based distillation residue, including distiller's wet grains (DWG), distiller's dry grains (DDG), dried distiller's grains with solubles (DDGS), and corn-based grain stillage syrup. Typically, DWG contains greater than about 65% moisture, and DDG often contains from about 10% to about 50% moisture. Stillage syrup usually has from about 20 to about 40% solids. It has been found that these and other biomass fermentate separation residues offer advantages when forming liquid transportation fuel components according to

embodiment of the invention, since such residues have idea H/C ratios, e.g., usually around 2:1.

[0026] In accordance with embodiments of the invention, a feed comprising biomass fermentate separation residue is provided to gasification reactor; such gasification reactor (also referred to as a gasifier) will be described in greater detail hereinunder. In some embodiments, the step of "providing" a feed may comprise a treatment step performed upon the biomass fermentate separation residue, prior to its being fed to a gasification reactor. Such a treatment step may be selected from one or more of pyrolysis, catalytic conversion, drying, concentrating, and charring; and the like. Each of these treatment steps may be capable of rendering biomass fermentate separation residue into a state more suitable for gasification. For instance, owing to a relatively high moisture content, a biomass fermentate separation residue such as DWG should be dried and/or concentrated prior to being fed to a gasifier, so as to enhance the efficiency of the reactor and avoid agglomeration or other deleterious effects of the moisture. In other embodiments, it may be advantageous to pyrolyze biomass fermentate separation residue in the substantial absence of oxygen, in order to convert at least a portion of the residue to a bio-oil or a char, either of which can then fed to a gasifier. In yet further embodiments, a catalytic conversion of biomass fermentate separation residue may be performed, to convert the residue to a form more suitable for gasification (e.g., more solids and/or higher carbon content and/or less tarry character).

[0027] In some other embodiments, the step of "providing" a feed comprising a biomass fermentate separation residue may simply comprise conveying or feeding a biomass fermentate separation residue to a gasifier, without any of the treatment steps noted above. Regardless of the nature of how the feed comprising a biomass fermentate separation residue is provided, the present disclosure also encompasses embodiments where the biomass fermentate separation residue is combined with a supplemental feed member, such as another biomass-based material (e.g., corn stover) and/or carbonaceous fuel. In certain cases, biomass fermentate separation residue is combined or mixed with at least one supplemental feed member selected from low rank coal, liquid

hydrocarbonaceous fuel, coke, oil shale, tar sands, asphalt, pitch, another biomass-based material, and mixtures thereof; and the like. The combining or mixing may occur within a gasifier, or more usually, prior to being fed to a gasifier.

[0028] It may be especially advantageous to employ low rank coals as the supplemental feed member to be combined with biomass fermentate separation residue. Coals having a "low rank" are generally understood by persons skilled in the art to typically be those coals having a lower grade than bituminous, e.g., sub-bituminous or lignitic coal. In some case, such low rank coals may have a relatively high oxygen content, such as from about 16% to 25% by weight. Other characteristics of low rank coals may include a relatively high moisture content, such as in the range of about 10% to 40%, and a relatively high dry ash content, such as in the range of about 12% to 40%. Low rank coals are present in abundance in the mid-continent region of the United States (as Powder River Basin coal), and in China (as brown coal).

[0029] Where a supplemental feed member is employed, the biomass fermentate separation residue may be directly combined therewith, or one or more of the aforementioned treatment steps (e.g., pyrolysis, catalytic conversion, drying, concentrating, charring) is performed upon a biomass fermentate separation residue prior to mixing with the supplemental feed member.

[0030] Regardless of how the feed is obtained or prepared, (e.g., whether or not biomass fermentate separation residue is mixed with a supplemental feed member and/or is pretreated in a treatment step), the feed is gasified in a gasification reactor to produce a mixture comprising at least carbon monoxide and hydrogen. As is generally known, the term gasification refers to a process which converts carbonaceous and/or hydrocarbon feedstocks into a synthesis gas (also known as syngas) comprising hydrogen and carbon monoxide. In a typical gasification plant, (1) a carbonaceous feedstock and (2) air, oxygen, steam, water and/or CO₂; are contacted within a gasification reactor, where partial oxidation of the feedstock occurs. The feedstock and molecular oxygen react and form syngas. Non-gasifiable ash material and unconverted and/or incompletely converted feedstock are by-products of the process. In some case, a quench process is used to cool

and saturate the syngas.

[0031] In accordance with embodiments of the invention, a gasification reactor may suitably be one or more type, such as fixed bed, bubbling bed, fluidized bed, entrained flow gasifier; or the like. Furthermore, the gasification reactor may have at least one characteristic selected from slurry-fed, pressurized, slagging; or the like. For example, in an entrained flow gasifier, gasifying agents such as oxygen, air, steam, or combination of these, are used to fluidize the feedstock and carry it at least some distance through the gasification reactor. Each of these types of gasification reactors and operating modes are per se known for use in generating syngas from coal, for instance.

[0032] In some embodiments, the gasification reactor can be operated in a pressurized mode (which can be any pressure above atmospheric but is typically between about 10 bar and about 40 bar), which may in certain cases afford good overall efficiencies. In some embodiments, the gasification reactor may instead be operated at substantially atmospheric pressure. In certain embodiments, one may operate the gasification reactors at temperatures higher than about 1000°C, e.g., from about 1000°C to about 1400°C, to more effectively gasify tarry components of the feed. However, operation at such high temperatures could require use of expensive refractory materials in the gasification reactor. In yet another embodiment the gasification reactor is operated at moderate temperatures, typically from about 700°C to about 1000°C.

[0033] Although step (a) through (d) are noted as process steps for the present integrated method for producing fuel from biomass, this is not to be taken to exclude the presence or use of other steps, to be described hereinafter. For instance, the mixture of CO and hydrogen generated in the gasification reactor in step (b) may also undergo further treatment steps such as scrubbing to remove acidic gases; or water-gas shifting to adjust the CO/hydrogen ratio. A step of adjusting the CO/H₂ ratio in a mixture can be accomplished by an adjusting step selected from one or more of: selective removal of CO, selective removal of hydrogen, water-gas shift, reverse-water-gas-shift; or the like. In cases where selective removal of CO or selective removal of hydrogen is desired, it may be performed by selective oxidation or by membrane processing. Adjusting the

CO/H₂ ratio in the mixture may promote the formation of desired products in the effluent of the hydrocarbon synthesis reactor, as explained in further detail below.

[0034] According to embodiments of the invention, it is typical that raw product syngas from gasification reactors further comprises other gaseous components as impurities in addition to CO and hydrogen. These impurities may include CO₂, NH₃, H₂S, HCN, HCl, COS, nitrogen, mercury, and the like. Such other gaseous components may be deleterious to downstream processing steps (e.g., hydrocarbon synthesis) performed upon the mixture, or may lessen the efficiency of these downstream processing steps. Therefore, in some embodiments, methods of the present disclosure further comprise an additional step of scrubbing or otherwise at least partially removing at least one impurity selected from ammonia, carbon dioxide, hydrogen sulfide, HCl, hydrogen cyanide, mercury, nitrogen and carbonyl sulfide from the mixture comprising CO and H₂ prior to contacting the mixture with the hydrocarbon synthesis catalyst. Scrubbers may be suitably employed for the acidic gaseous impurities (e.g., CO₂ and H₂S), while guard beds may be used for mercury removal. In embodiments where carbon dioxide is separated and recovered from the raw product syngas, carbon dioxide may in certain cases be sequestered so as to limit emission of climate-change suspect compounds.

[0035] In embodiments of the invention, a gaseous mixture comprising CO and H₂ (suitably scrubbed of impurities and adjusted in CO/H₂ ratio, as appropriate), is passed to a synthesis reactor in which contact is made with a hydrocarbon synthesis catalyst, to produce heat and an effluent comprising a liquid transportation fuel component. Such a hydrocarbon synthesis catalyst may comprise any of the catalytic materials heretofore known for hydrocarbon synthesis by the Fischer-Tropsch (F-T) reaction, such as at least one selected from Fe, Co, Ni, Re, Ru; and the like. These catalytic materials may be provided in elemental and/or compound form. Typically, these catalytic materials may be provided and used in dispersed form and supported upon an inorganic support material, such as a refractory inorganic support material, e.g., zirconia, titania, or alumina. Often, the catalytic materials of the hydrocarbon synthesis catalyst of the present embodiments further comprises one or more promoter material. In some embodiments, the hydrocarbon

synthesis catalyst comprises one or more of Fe, Co, Ni, Re, Ru present in an amount of from about 1% to about 50% by weight of total hydrocarbon synthesis catalyst. Where the hydrocarbon synthesis catalyst comprises at least one selected from Fe, Co, Ni, Re, Ru, then any one or more of the following may be employed as co-catalysts or promoters: Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg and La; and the like. Often, use of Co as catalyst material promotes the formation of paraffins.

[0036] In embodiments of the invention, a gaseous mixture comprising CO and H₂ is contacted with a hydrocarbon synthesis catalyst under conditions of temperature such as between about 140°C to about 400°C (or more narrowly, between about 200°C to about 250°C); and at conditions of pressure such as between about 0.5 to about 50 bars (or more narrowly, between about 2 to about 25 bars). Note that here (as elsewhere in this disclosure), all ranges disclosed are inclusive of the recited endpoint and are independently combinable.

[0037] The hydrocarbon synthesis reactor may be one or more of a variety of reactor types; for example, fixed bed reactors containing one or more catalyst beds, slurry reactors, fluidized bed reactors, or a combination of different type reactors. In some embodiments, the hydrocarbon synthesis process is a slurry Fischer-Tropsch process, in which a syngas comprising a mixture of H₂ and CO is bubbled up through a slurry in a reactor which comprises a particulate hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid at the reaction conditions.

[0038] In accordance with some embodiments of the invention, the contact of syngas with the hydrocarbon synthesis catalyst in the synthesis reactor results in an effluent comprising one or more liquid transportation fuel component. Such a "liquid transportation fuel component" (which usually comprises at least paraffins) may itself be used as a liquid transportation fuel, or may be suitably blended with another fuel and/or additive to be useful as a liquid transportation fuel. Therefore, the term "component" is employed to signify that the effluent from the synthesis reactor may be used as part of a liquid transportation fuel, or as a fuel itself (after any appropriate separation and/or

hydroprocessing, as explained more fully below). For instance, in certain embodiments, methods and systems herein provide a liquid transportation fuel component that has sufficient lubricity and other parameters such that it can be used as a jet turbine fuel. In alternative embodiments, liquid transportation fuel components require admixture with other fuels and/or additives in order to be useful as a jet turbine fuel. As used herein a "liquid transportation fuel" and a "liquid transportation fuel component" generally refers to hydrocarbonaceous fuels boiling within the range of gasoline, jet fuel, kerosene, or diesel. In some embodiments, the liquid transportation fuel component may be used as a turbine fuel. The formation of a desired type of liquid transportation fuel component may be promoted by: (1) choosing the proper chemical composition for the feed comprising biomass fermentate separation residue; (2) adjusting the CO/H₂ ratio of the syngas formed in the gasification reactor; (3) adjusting conditions including temperature, pressure, and/or catalyst in the hydrocarbon synthesis reactor; and (4) combinations of the foregoing. For instance, the H/C ratio in dried distiller's grains may be ideal for conversion into (e.g., paraffinic) liquid transportation fuel components.

[0039] A "turbine fuel" refers to a fuel composition which may be burned in a turbine to provide power. Turbines may be stationary, such as those used to generate electricity, or they may be used to power mobile platforms, such as providing power for ships or airplanes. Turbine fuels meeting certain specifications may be used as jet fuel for airplanes. Specifications for turbine fuel intended for use in jet engines are more stringent than those for fuels intended for use in turbines used to produce electricity.

[0040] As is generally known, a "jet fuel" is a material suitable for use in aviation turbines and typically meets the current version of at least one of the following specifications: ASTM D1655; DEF STAN 91-91/3 (DERD 2494); International Air Transportation Association (IATA) "Guidance Material for Aviation Turbine Fuels Specifications", 4th edition, March 2000 ; United States military jet fuel specifications MIL-DTL-5624; and MIL-DTL-83133; and variants thereof. Also known as aviation turbine fuel, jet fuel is an aviation fuel with various specified grades such as Jet-A, JP-A, JP-B, JP-4, JP-5, JP-7, JP-8, JP8+100, and the like. Jet fuel is a special grade of

kerosene; the specifications of various grades are specified by various standards. As an example, JP-8 is defined by standard MIL-T-83133C.

[0041] Where the liquid transportation fuel component according to embodiments of the invention is to be used for aviation turbine or jet fuel purposes, it generally meets one or more of the following parameters: an H/C ratio of greater than about 1.85, more narrowly, between about 1.85 and about 2.20; a flash point of at least about 38°C, more narrowly, from about 38°C to about 60°C, and even more narrowly from about 40°C to about 60°C; and a freeze point of less than about -40°C, more narrowly less than about -47°C, often having an average freeze point of from about -50°C to about -60°C (freeze point as defined by ASTM-D-2386). In some embodiments of the invention, the liquid transportation fuel component additionally meets one or more of the jet fuel standard specifications noted previously.

[0042] In some embodiments, various additives such as antioxidants, antistatic agents, corrosion inhibitors, icing inhibitors, etc., may be added to the liquid transportation fuel component, before it is used in transportation, e.g., before it is used as jet fuel or aviation turbine fuel. The amount and type of additives may be different for different grades of transportation fuel.

[0043] In accordance with some other embodiments of the invention, the contact of syngas with the hydrocarbon synthesis catalyst in the synthesis reactor results in an effluent comprising one or more liquid transportation fuel component, where the liquid transportation fuel component is thereafter upgraded by hydroprocessing. This additional hydroprocessing step is generally selected from one or more of hydrocracking, hydrotreating, and isomerization; and the like. Such hydroprocessing steps per se are generally known to persons of skill in the art of hydrocarbon processing. Hydroprocessing may usually be carried out in the presence of free hydrogen, for removal of alcohols and hydrogenation of olefins present in the effluent. In some cases, upgrading by hydroprocessing may be performed upon some or all of the liquid transportation fuel component, in order to impart desired properties. For instance, a liquid transportation fuel component in accordance with some embodiments of the present

invention, can be upgraded by hydroprocessing to be suitable for use as aviation turbine fuel.

[0044] In still further embodiments of the invention, the effluent from the hydrocarbon synthesis reactor comprising one or more liquid transportation fuel component may be separated by one or more distillation or other separation process. Usually, such distillation or separation will be on the basis of boiling point. Thus, the effluent comprising one or more liquid transportation fuel component may be distilled into one or more lower boiling fractions and one or more higher boiling fractions. It may be advantageous to perform such distillation to separate liquid fuel components from waxy fuel components. Finally, both distillation and hydroprocessing, in any order, may be performed upon effluent from the hydrocarbon synthesis reactor.

[0045] As previously noted, integrated methods according to embodiments of the invention, comprise supplying at least a portion of heat produced by the hydrocarbon synthesis step to at least one thermal process which requires heat, selected from biomass liquefaction, fermentation, fermentation product distillation, dehydrating agent regeneration, fermentate separation residue concentrating, and fermentate separation residue drying. More particularly, the heat produced by the hydrocarbon synthesis step is supplied to at least two, or at least three, or at least four, or at least five, of said thermal processes. Although each of these processes which require heat is denoted as a "thermal process", this is not to indicate that only thermal or physical processes occur; each of these processes may also additionally comprise chemical and/or biochemical process. For instance, a biomass liquefaction process can be a ground corn cooking process whereby corn meal is heated in the presence of moisture and an enzyme. Furthermore, although some of the steps of the methods may be parallel to other steps of the method, the term "integrated," as used herein, means that certain steps of the method are interrelated or dependent upon either earlier or later steps of the total method.

[0046] The heat which emanates from the synthesis reactor (e.g., Fischer-Tropsch reactor) may be recovered in many suitable ways, including heat recovery by indirect heat exchange with the synthesis reactor, either internal to the reactor or externally, or by

heat recovery from the hot effluent gases removed as product from the reactor. In typical hydrocarbon synthesis reactors, a stream can be removed (e.g., the overhead stream) that comprises water, among other components. Heat may be obtained from the hydrocarbon synthesis reactors by cooling the water-containing stream from the reactor, or by cooling the reactor itself, or by cooling other effluent streams from the reactor. More specifically, one or more hot effluent stream from the hydrocarbon synthesis reactor may be passed through a heat exchanger. A usable heat exchanger can be a shell and tube heat exchanger or a welded plate and frame heat exchanger. Alternatively, the synthesis reactor may contain cooling coils, which serve to remove heat generated during the highly exothermic Fischer-Tropsch reaction. Both cooling coils internal to the hydrocarbon synthesis reactor, and heat exchangers for heat removal from hot effluent streams, can be used simultaneously.

[0047] In order to supply the heat from the hydrocarbon synthesis reactor to the thermal processes which require heat, one may suitably employ conventional means. Use of heat transfer fluids such as steam or heated air or other heated gas are well known and effective means for supplying recovered heat to where it is required.

[0048] Referring now to Figure 3, here is shown a schematic diagram of an exemplary (but non-limiting) mode of removing heat from a hydrocarbon synthesis reactor and supplying it to one or more thermal processes. Fischer-Tropsch reactor 300 is fed with a syngas through line 30, and an effluent comprising a liquid transportation fuel component is recovered through 31. Cooling water in line 32 is fed through cooling coils within reactor 300 to make indirect heat contact with the hot reactor, and the steam raised by this process is supplied to drive the one or more thermal processes 109.

[0049] Thermal processes which requires heat are selected from one or more of biomass liquefaction, fermentation, fermentation product distillation, dehydrating agent regeneration, fermentate separation residue concentrating, and fermentate separation residue drying. The integrated systems and methods disclosed herein may obviate or reduce the necessity to import energy to drive these thermal processes. For example, fermentate separation residue drying (e.g., drying distiller's grains) has been typically

performed using natural gas fired burners in the prior art. This can increase costs for producing ethanol from corn. However, the present methods and systems may offer the advantage of cost savings by recycling a form of waste heat.

[0050] A biomass liquefaction process may comprise enzymatic and/or bacterial decomposition of any of the biomass materials noted previously. An exemplary but non-limiting type of biomass liquefaction may be the previously-described process where milled corn is mixed with water and an enzyme, and then passed to cookers to liquefy starch into a mash. Heat is usually required to enhance liquefaction.

[0051] A fermentation process may comprise enzymatic, bacterial, and/or yeast-mediated production of an alcohol from a biomass material. An exemplary but non-limiting type of fermentation process can include the previously-described process for recovery of ethanol from corn mash fermentation. Fermentation processes benefit from heat input.

[0052] A fermentation product distillation process typically comprises distillation of a fermentate to separate an alcohol. One non-limiting example of a fermentation product distillation process is the distillation of fermented corn mash to recover ethanol as a fermentation product. A fermentation product distillation process usually requires heat to drive the production of the desired alcohol, e.g., azeotropic ethanol.

[0053] A dehydrating agent regeneration process generally comprises regeneration of a spent solid dehydrating agent. Usually, such a spent solid dehydrating agent has been used to dehydrate a biomass fermentation product (e.g., ethanol from corn fermentation). The most accepted approach to dehydration of ethanol now used industrially is to use adsorption by molecular sieves as solid dehydrating agent, such as zeolite 3A. Typically a two bed system is used in which one bed of solid dehydrating agent receives a flow of azeotropic ethanol for dehydration and the other undergoes regeneration. Although in some instances regeneration of a bed containing spent solid dehydrating agent can occur under vacuum, in other cases heat can be used to drive off the water from the spent dehydrating agent and thus regenerate the agent.

[0054] A fermentate separation residue concentrating process generally comprises

reducing the volume of a fermentate separation residue. A "fermentate separation residue" can be the rejected residue after separation (e.g., distillation) of a desired product (e.g., an alcohol or other volatile organic compound) from a biomass (e.g., corn) fermentate. Such fermentate separation residue may include corn-based distiller's grains or distiller's syrup. Reduction in volume may be performed in a centrifuge. Heat may sometimes be employed to aid in volume reduction.

[0055] A fermentate separation residue drying process may include removing at least some moisture from a fermentate separation residue, such as drying corn-based distiller's grains in a dryer (e.g., a steam tube rotary or ring dryer). Often, for particular purposes, such residues require drying to a given moisture level prior to further utilization, e.g., prior to gasification or use as feed. In such cases, drying can be accomplished using conventional means, such as steam dryer, gas dryer, spray dryer, pneumatic conveying dryer, fluidized bed dryers, rotary kilns, or the like.

[0056] In some particular embodiments, the thermal process is used to generate, separate and/or treat the biomass fermentate separation residue; or the thermal process is used to treat another product of the same process which generates, separates and/or treats the biomass fermentate separation residue. Stated in other words: the thermal process to which heat is supplied may be a process that concentrates or dries the biomass fermentate separation residue that is sent to the "providing" step (a). For example, this would be the case where dried distiller's grains are converted into liquid transportation fuels, and the heat from hydrocarbon synthesis is used to dry these distiller's grains.

[0057] Alternatively, the thermal process may be a process that liquefies, ferments, or distills the biomass from which the biomass fermentate separation residue is derived. For example, this would be the case where heat from hydrocarbon synthesis from syngas is used to ferment, liquefy, or distill corn to make the distiller's grains which are gasified to make the syngas.

[0058] Alternatively, the thermal process may be one which treats another product of the same process which generates, separates and/or treats the biomass fermentate separation residue. For example, this would occur when heat from hydrocarbon synthesis

is used to regenerate a drying agent that has been used to dry ethanol, made in the same process that also makes distiller's grains.

[0059] Referring now to Figure 4, here is shown a block flow diagram, schematically setting forth variant methods in accordance with other embodiments of the invention. Both a supplemental feed member 34 comprising Powder River Basin coal, and a biomass fermentate separation residue 35, are supplied to a step of providing 400 a feed. As previously described, the step of "providing" 400 may comprise a pretreatment step such as pyrolysis, catalytic conversion, drying, concentrating, and/or charring (not specifically shown here). The step of providing 400 generates a provided feed 36. The provided feed 36 is then supplied to a gasifying step 401 in a gasification reactor, to produce a mixture 37 comprising CO and H₂. This mixture 37 is supplied (either directly or indirectly) to a contacting step 402 wherein the mixture 37 is contacted with a hydrocarbon synthesis catalyst in a synthesis reactor to produce heat 40 and an effluent 38 comprising at least paraffins. The effluent 38 is then upgraded in a hydroprocessing step 403 to produce a liquid transportation fuel component 39.

[0060] Heat 40 may be supplied to any one or more of six thermal processes 410, shown collectively in a dotted box. Each of the six thermal processes are biomass liquefaction 404, fermentation 405, fermentation product distillation 406, dehydrating agent regeneration 407, fermentate separation residue concentrating 408, and fermentate separation residue drying 409.

[0061] As used herein, approximating language may be applied to modify any quantitative representation that may vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about" and "substantially," may not be limited to the precise value specified, in some cases. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (for example, includes the degree of error associated with the measurement of the particular quantity). "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, or that the subsequently identified material may or may not be present, and that

the description includes instances where the event or circumstance occurs or where the material is present, and instances where the event or circumstance does not occur or the material is not present. The singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. All ranges disclosed herein are inclusive of the recited endpoint and independently combinable.

[0062] While the invention has been described in detail in connection with only a limited number of embodiments, it should be readily understood that the invention is not limited to such disclosed embodiments. Rather, the invention can be modified to incorporate any number of variations, alterations, substitutions or equivalent arrangements not heretofore described, but which are commensurate with the spirit and scope of the invention. Additionally, while various embodiments of the invention have been described, it is to be understood that aspects of the invention may include only some of the described embodiments. Accordingly, the invention is not to be seen as limited by the foregoing description, but is only limited by the scope of the appended claims.

[0063] What is claimed as new and desired to be protected by Letters Patent of the United States is:

CLAIMS

1. An integrated method for producing fuel from biomass, the method comprising the steps of:

- (a) providing a feed comprising biomass fermentate separation residue;
- (b) gasifying feed from (a) in a gasification reactor to produce a mixture comprising CO and H₂;
- (c) contacting the mixture comprising CO and H₂ with a hydrocarbon synthesis catalyst in a synthesis reactor to produce heat and an effluent comprising a liquid transportation fuel component; and
- (d) supplying at least a portion of said heat to at least one thermal process selected from the group consisting of biomass liquefaction, fermentation, fermentation product distillation, dehydrating agent regeneration, fermentate separation residue concentrating, and fermentate separation residue drying.

2. The method of claim 1, wherein at least a portion of said heat is supplied to a biomass liquefaction process comprising enzymatic and/or bacterial decomposition of biomass.

3. The method of claim 1, wherein at least a portion of said heat is supplied to a fermentation product distillation process comprising distillation of a fermentate to separate an alcohol.

4. The method of claim 1, wherein at least a portion of said heat is supplied to a fermentation process comprising enzymatic, bacterial, and/or yeast-mediated production of an alcohol.

5. The method of claim 1, wherein at least a portion of said heat is supplied to a dehydrating agent regeneration process comprising regeneration of a spent solid dehydrating agent.
6. The method of claim 1, wherein at least a portion of said heat is supplied to a fermentate separation residue concentrating process comprising reducing volume of a fermentate separation residue.
7. The method of claim 1, wherein at least a portion of said heat is supplied to a fermentate separation residue drying process comprising removing at least some moisture from a fermentate separation residue.
8. The method of claim 1, wherein at least a portion of said heat is supplied to at least two of said thermal process.
9. The method of claim 1, wherein at least a portion of said heat is supplied to at least four of said thermal process.
10. The method of claim 1, wherein said biomass fermentate separation residue is derived from fermentation of at least one plant biomass selected from the group consisting of woody materials, forest residues, agricultural residues and crops.
11. The method of claim 1, wherein said biomass fermentate separation residue is at least one corn-based material selected from distiller's wet grains (DWG), distiller's dry grains (DDG), dried distiller's grains with solubles (DDGS), and corn-based grain stillage syrup.
13. The method of claim 1, wherein said step of providing a feed comprises performing one or more treatment selected from the group consisting of pyrolysis,

catalytic conversion, drying, concentrating, and charring upon a biomass fermentate separation residue.

14. The method of claim 1, further comprising one or more step of adjusting the CO/H₂ ratio in said mixture comprising CO and H₂ by an adjusting step selected from one or more of: selective removal of CO, selective removal of hydrogen, water-gas shift, and reverse-water-gas-shift.

15. The method of claim 1, further comprising an additional step of at least partially removing at least one impurity selected from the group consisting of CO₂, NH₃, H₂S, HCN, HCl, COS, N₂ and Hg from the mixture comprising CO and H₂ prior to contacting said mixture with the hydrocarbon synthesis catalyst.

16. The method of claim 1, further comprising an additional step of treating at least of portion of said effluent comprising a liquid transportation fuel component by a hydroprocessing step selected from one or more of hydrocracking, hydrotreating, and isomerization.

17. The method of claim 1, wherein said step of providing a feed comprises mixing biomass fermentate separation residue with at least one supplemental feed member selected from the group consisting of low rank coal, liquid hydrocarbonaceous fuel, coke, oil shale, tar sands, asphalt, pitch, another biomass-based material, and mixtures thereof.

18. The method of claim 1, wherein the gasification reactor is a fixed bed, bubbling bed, fluidized bed, or entrained flow gasifier.

19. The method of claim 1, wherein said liquid transportation fuel component is a hydrocarbonaceous fuel having a boiling point within the range of gasoline, jet fuel, kerosene, or diesel fuel.

20. The method of claim 19, wherein said liquid transportation fuel component is an aviation turbine fuel having at least one characteristic selected from H/C ratio of greater than about 1.85, flash point of at least about 38°C, and average freeze point of less than about -40°C.

21. An integrated method for producing a turbine fuel from corn-based biomass, the method comprising the steps of:

(a) providing a feed comprising corn-based biomass fermentate distillation residue;

(b) gasifying feed from (a) in a gasification reactor to produce a mixture comprising CO and H₂;

(c) contacting the mixture comprising CO and H₂ with a hydrocarbon synthesis catalyst in a synthesis reactor to produce heat and an effluent comprising a liquid turbine fuel component; and

(d) supplying at least a portion of said heat to at least three thermal processes selected from the group consisting of corn liquefaction, corn mash fermentation, corn fermentation product distillation, corn-based ethanol dehydrating agent regeneration, corn mash fermentate distillation residue concentrating, and corn mash fermentate distillation residue drying.

22. An integrated system for producing fuel from biomass, the system comprising,

(a) a unit configured to provide a feed comprising biomass fermentate separation residue;

(b) a gasification reactor for gasifying feed from (a) to produce a mixture comprising CO and H₂;

(c) catalytic hydrocarbon synthesis zone configured to react the mixture comprising CO and H₂ to produce heat and an effluent comprising a liquid transportation fuel component; and

(d) at least one heat supply conduit configured to supply at least a portion of said heat to at least one thermal process selected from the group consisting of biomass liquefaction, fermentation, fermentation product distillation, dehydrating agent regeneration, fermentate separation residue concentrating, and fermentate separation residue drying.

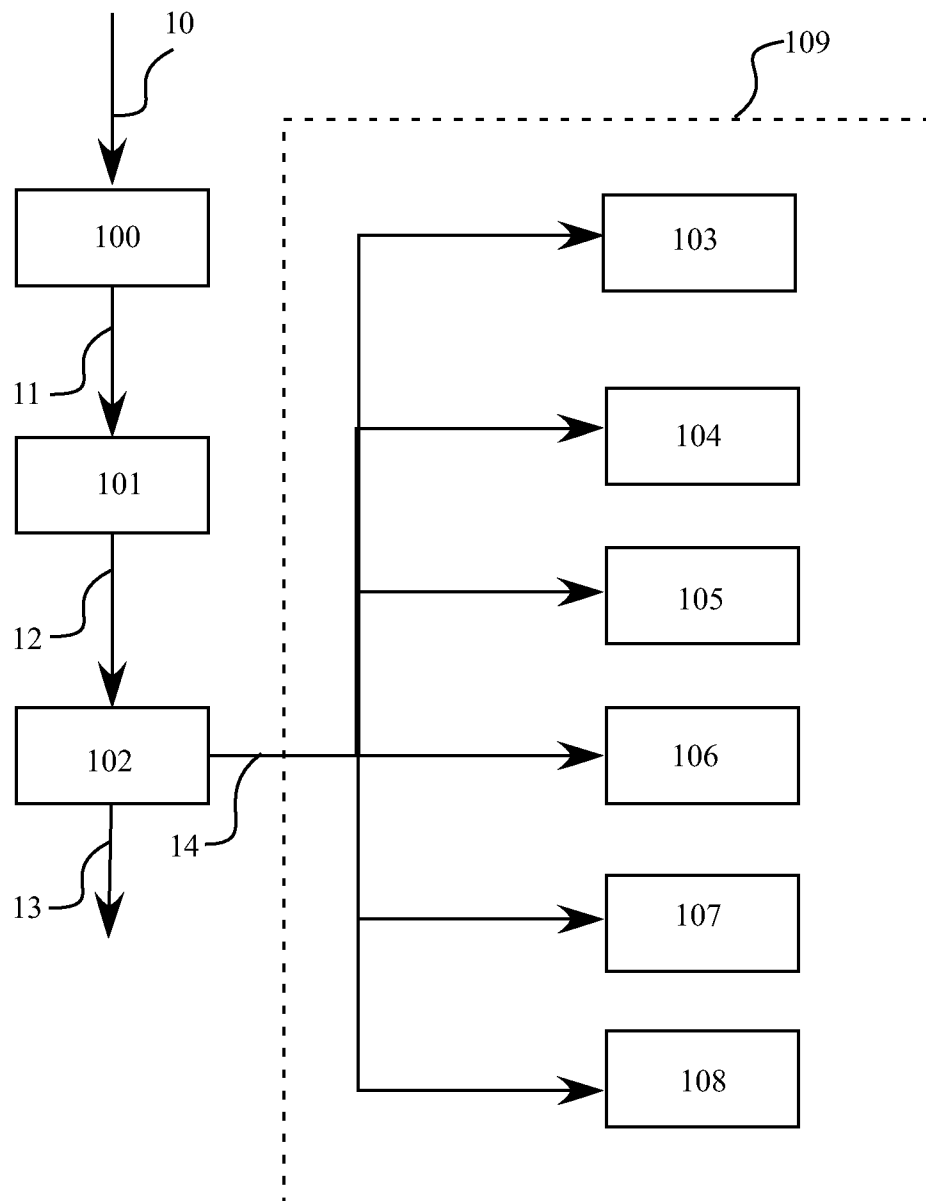


Figure 1

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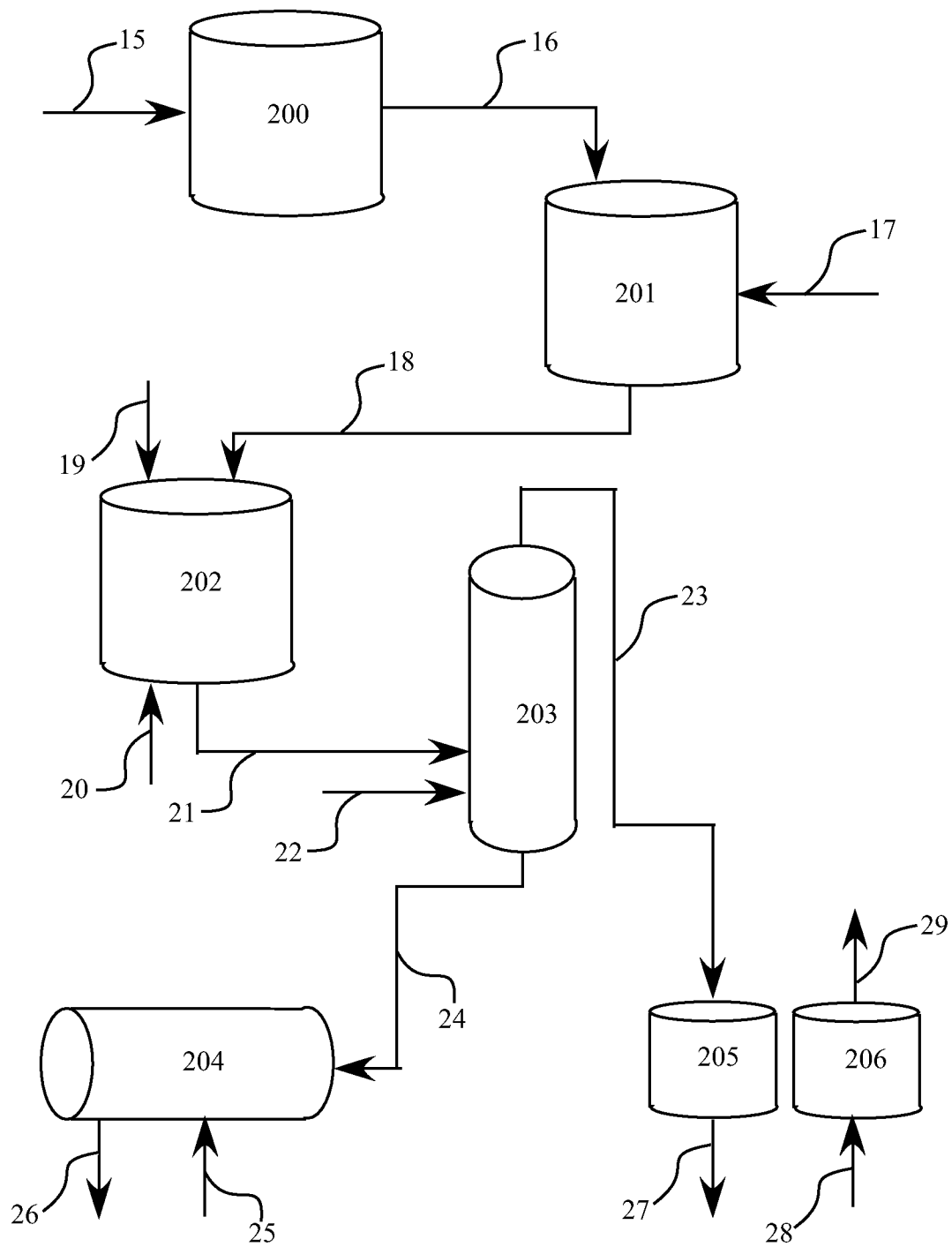


Figure 2

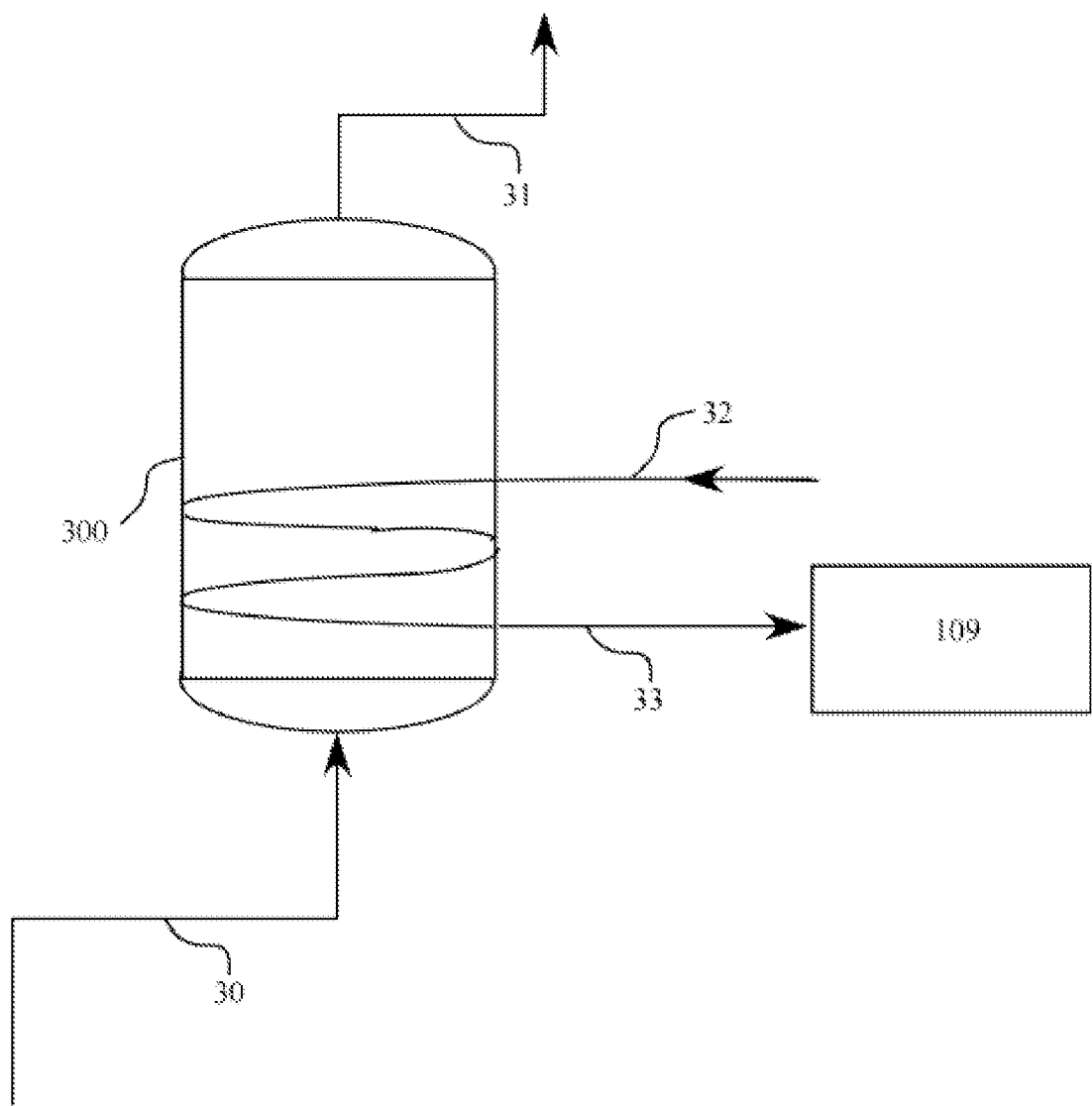


Figure 3

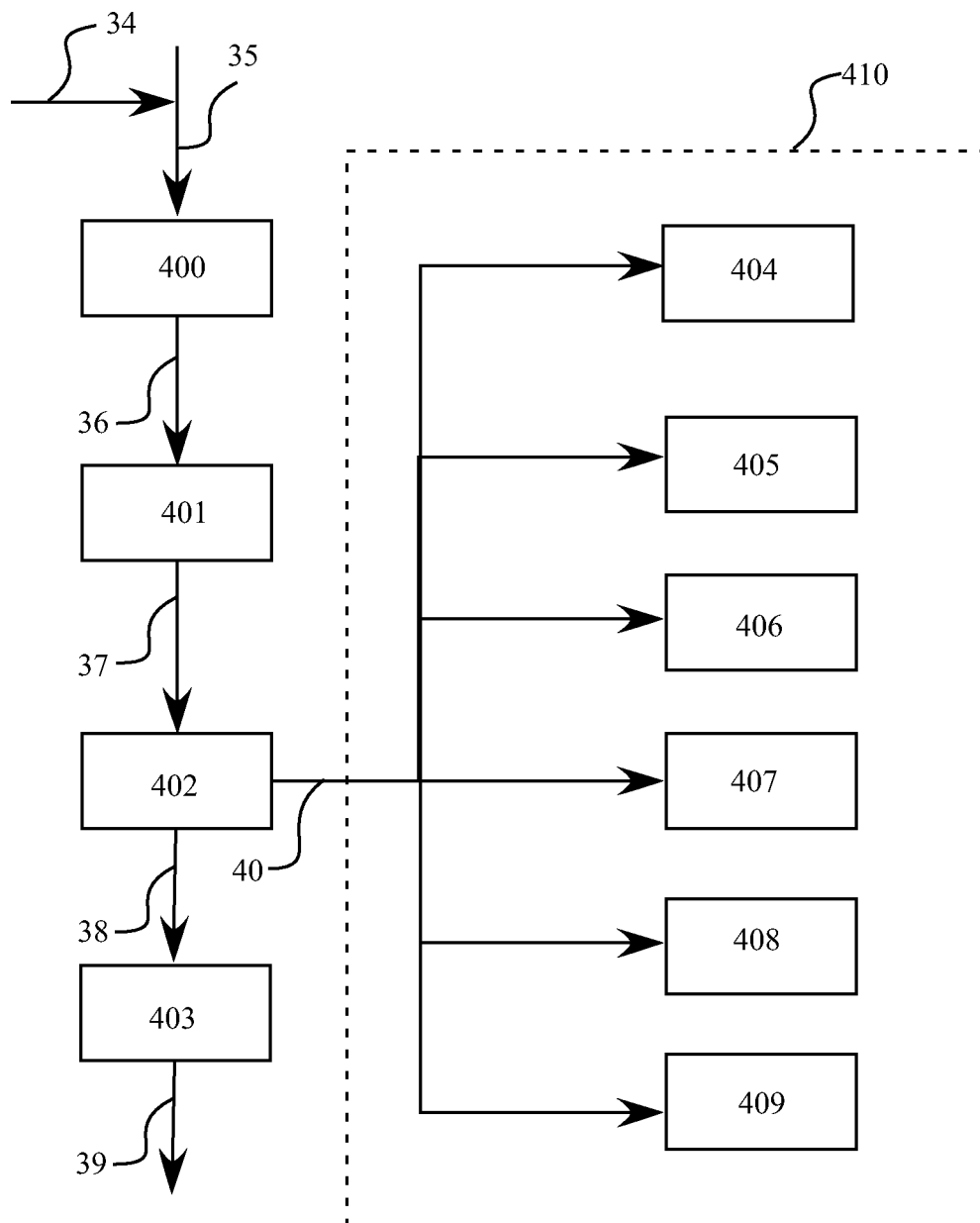


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/071883**A. CLASSIFICATION OF SUBJECT MATTER***C10J 3/00(2006.01)i, C10J 3/46(2006.01)i, C10L 3/06(2006.01)i*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 C10J 3/00, C10J 3/46, C10L 3/06, C07C 31/04, B09B 3/00, C02F 11/04, C10B 53/00, B09B 3/00

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

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

e-KIPASS (KIPO internal) and keywords: biomass, gas, heat, supply, source, exchange, catalyst, fermentate, residue, and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2004-249247 A (KANGEN YOYU GIJUTSU KENKYUSHO) 9 SEPTEMBER 2003 See abstract, claims 1, 2, 11, and paragraph 0012	1-22
A	JP 2005-205385 A (KANGEN YOYU GIJUTSU KENKYUSHO) 4 AUGUST 2005 See abstract, claim 1, and paragraph 7	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

31 OCTOBER 2008 (31.10.2008)

Date of mailing of the international search report

31 OCTOBER 2008 (31.10.2008)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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