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(54) Titre : TRAITEMENT D'UNE BIOMASSE A L'AIDE D'UNE SOURCE D'HYDROGENE
(54) Title: PROCESSING BIOMASS WITH A HYDROGEN SOURCE

(57) Abrégé/Abstract:
A method can include co-processing a biomass feedstock and a refinery feedstock in a refinery unit. The method can include producing a liquid product by catalytically cracking a biomass feedstock and a refinery feedstock in a refinery unit having a fluidized reactor. Catalytically cracking can include transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock.

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(54) Title: PROCESSING BIOMASS WITH A HYDROGEN SOURCE

(57) Abstract: A method can include co-processing a biomass feedstock and a refinery feedstock in a refinery unit. The method can include producing a liquid product by catalytically cracking a biomass feedstock and a refinery feedstock in a refinery unit having a fluidized reactor. Catalytically cracking can include transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock.

PROCESSING BIOMASS WITH A HYDROGEN SOURCE

FIELD OF THE INVENTION

[0001] The invention relates to producing a fuel or specialty chemical product from biomass through a chemical process. The invention relates more particularly to converting biomass together with a hydrogen source into a fuel, specialty chemical, and/or intermediate product.

BACKGROUND OF THE INVENTION

[0002] Biomass, in particular biomass of plant origin, is recognized as an abundant potential source of fuels and specialty chemicals. See, for example, "Energy production from biomass," by P. McKendry - Bioresource Technology 83 (2002) P 37-46 and "Coordinated development of leading biomass pretreatment technologies" by Wyman et al., Bioresource Technology 96 (2005) 1959-1966. Refined biomass feedstock, such as vegetable oils, starches, and sugars, can be substantially converted to liquid fuels including biodiesel (e.g., methyl or ethyl esters of fatty acids) and ethanol. However, using refined biomass feedstock for fuels and specialty chemicals can divert food sources from animal and human consumption, raising financial and ethical issues.

[0003] Alternatively, inedible biomass can be used to produce liquid fuels and specialty chemicals. Examples of inedible biomass include agricultural waste (such as bagasse, straw, com stover, com husks, and the like) and specifically grown energy crops (like switch grass and saw grass). Other examples include trees, forestry waste, such as wood chips and saw dust from logging operations, or waste from paper and/or paper mills. In addition, aquacultural sources of biomass, such as algae, are also potential feedstocks for producing fuels and chemicals. Inedible biomass generally includes three main components: lignin, amorphous hemi-cellulose, and crystalline cellulose. Certain components (e.g., lignin) can reduce the chemical and physical accessibility of the biomass, which can reduce the susceptibility to chemical and/or enzymatic conversion.

[0004] Attempts to produce fuels and specialty chemicals from biomass can result in low value products (e.g., unsaturated, oxygen containing, and/or annular hydrocarbons). Although such low value products can be upgraded into higher value products (e.g., conventional gasoline, jet fuel), upgrading can require specialized and/or costly conversion processes and/or refineries, which are distinct from and incompatible with conventional

petroleum-based conversion processes and refineries. Thus, the widespread use and implementation of biomass to produce fuels and specialty chemicals faces many challenges because large-scale production facilities are not widely available and can be expensive to build. Furthermore, existing processes can require extreme conditions (e.g., high temperature and/or pressure, expensive process gasses such as hydrogen, which increases capital and operating costs), require expensive catalysts, suffer low conversion efficiency (e.g., incomplete conversion or inability to convert lignocellulosic and hemi-cellulosic material), and/or suffer poor product selectivity.

BRIEF SUMMARY OF THE INVENTION

[0005] In various embodiments, the invention includes methods, apparatuses, kits, and compositions for converting cellulosic (e.g., including ligno-cellulosic and hemicellulosic) material in biomass (e.g., including edible and inedible portions) into fuels and/or specialty chemicals under conditions that can mitigate equipment cost, energy cost, and/or degradation or undesirable reaction of conversion product. Examples of fuels include light gases (e.g., ethane, propane, butane), naphtha, and distillates (e.g., jet fuel, diesel, heating oil). Examples of chemicals include light olefins (e.g., ethylene, propylene, butylenes), acids (e.g., formic and acetic), aldehydes, alcohols (e.g., ethanol, propanol, butanol, phenols), ketones, furans, and the like. For example, the invention includes co-processing a biomass feedstock and a refinery feedstock (or, more generally, a hydrogen donor), which can improve conversion of the biomass into fuels and/or specialty chemicals in conventional petroleum refining processes (e.g., a known refinery unit). The invention also includes adapting existing refinery processes for co-processing biomass feedstock (e.g., change operating parameters, catalyst, and feedstock), retrofitting existing refinery process units for processing biomass (e.g., adding an extra riser for biomass catalytic cracking or adding a solid biomass feeder system to introduce biomass), and constructing new, purpose-built biomass reactors (e.g., employ commercially available conventional reactor components). Thus, the methods, apparatuses, kits, and compositions can reduce the cost and increase the availability of fuel and/or specialty chemicals derived from biomass.

[0006] In one aspect, the invention features a method for co-processing a biomass feedstock and a refinery feedstock in a refinery unit. The method includes producing a liquid product by catalytically cracking a biomass feedstock and a refinery feedstock in a refinery unit having a

fluidized reactor. Catalytically cracking includes transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock.

[0007] In another aspect, the invention features a method for co-processing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas in a refinery unit. The method includes producing a liquid product by hydrocracking or hydrotreating a biomass feedstock and a refinery feedstock in the presence of hydrogen gas in a refinery unit having a hydrocracking or hydrotreating reactor. Hydrocracking or hydrotreating comprises transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock.

[0008] In yet another aspect, the invention features a refinery unit for co-processing a biomass feedstock and a refinery feedstock. The refinery unit includes a fluidized reactor; a first system providing a biomass feedstock and a refinery feedstock to the fluidized reactor; and a second system for at least one of refreshing and regenerating a catalyst for the fluidized reactor. The first system and the second system support catalytic cracking including transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock within the fluidized reactor.

[0009] In still another aspect, the invention features a method for providing a refinery unit for co-processing a biomass feedstock and a refinery feedstock. The method includes providing a fluidized reactor; providing a first system providing a biomass feedstock and a refinery feedstock to the fluidized reactor; and providing a second system for at least one of refreshing and regenerating a catalyst in the fluidized reactor. The first system and the second system support catalytic cracking comprising transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock within the fluidized reactor.

[0010] In another aspect, the invention features a refinery unit for co-processing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas. The refinery unit includes a hydrocracking or hydrotreating reactor; a first system providing a biomass feedstock, a refinery feedstock, and hydrogen gas to the hydrocracking or hydrotreating reactor; and a second system for at least one of refreshing and regenerating a catalyst in the hydro cracking or hydrotreating reactor. The first system and the second system support hydro cracking or hydrotreating comprising transferring hydrogen from the hydrogen gas to carbon and oxygen

from the biomass feedstock and to carbon from the refinery feedstock in the hydrocracking or hydrotreating reactor.

[0011] In yet another aspect, the invention features a method for providing a refinery unit for co-processing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas. The method includes providing a hydrocracking or hydrotreating reactor; providing a first system providing a biomass feedstock, a refinery feedstock, and hydrogen gas to the hydrocracking or hydrotreating reactor; and providing a second system for at least one of refreshing and regenerating a catalyst in the hydrocracking or hydrotreating reactor. The first system and the second system support hydrocracking or hydrotreating comprising transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock in the hydrocracking or hydrotreating reactor.

[0012] In other examples, any of the aspects above, or any method, apparatus, or composition of matter described herein, can include one or more of the following features. Method steps can be performed in the order presented, as well as in any other combinations or number of iterations.

[0013] In various embodiments, the method can include increasing liquid product yield by increasing H_20 formation relative to at least one of CO and CO2 formation.

[0014] In some embodiments, the method can include operating the refinery unit at a site adjacent to a solid biomass growth source.

[0015] In certain embodiments, the biomass feedstock includes a plurality of solid biomass particles. The plurality of solid biomass particles can be substantially characterized by an average size between about 50 and about 750 microns and individual sizes between about 0.1 and about 1000 microns. The plurality of solid biomass particles can be substantially characterized by an average size between about 50 and about 1000 microns and individual sizes between about 0.1 and about 1500 microns. The plurality of solid biomass particles can be substantially characterized by at least about 80% of the particles having individual sizes of about 10 microns or less. The biomass feedstock can include a catalyst is in mechano-chemical interaction with at least a portion of the solid biomass particles. The biomass

feedstock can include a heavy liquid fraction of a liquefied biomass feedstock. The biomass feedstock can be substantially free of mineral contamination capable of inactivating a catalyst.

[0016] In various embodiments, the refinery unit includes a system for at least one of refreshing and regenerating a catalyst.

[0017] In some embodiments, the refinery feedstock includes one or more of an atmospheric gas oil or a vacuum gas oil from a paraffinic or naphthenic crude source, a resid from a paraffinic or naphthenic crude source, a hydrotreated vacuum gas oil, a hydro treated resid, and a hydro treated light cycle oil.

[0018] In certain embodiments, the method includes using a basic catalyst. The method can include using a zeolite catalyst. The method can include using one or more of a hydrotreating, hydro cracking, hydrogenation, NiMo, CoMo, NiCoMo, noble metal, and supported noble metal catalyst. The method can include using a water-insoluble catalyst. The method can include using a solid base catalyst comprising hydrotalcite; hydrotalcite-like material; clay; layered hydroxy salt; mixed metal oxide; a calcinations product of any of these materials; or a mixture thereof. The method can include using an alumina catalyst. The method can include using a fluid catalytic cracking catalyst. The method can include using a petroleum coke catalyst.

[0019] In various embodiments, reactor includes a bed reactor. The reactor can include a transport reactor. The reactor can include a riser reactor. The reactor can include a downer reactor.

[0020] In some embodiments, the method includes a reaction time of about 2 seconds or less. The method can include a reaction time that favors kinetic products relative to equilibrium products.

[0021] In certain embodiments, the method includes de-mineralizing the biomass feedstock. The method can include torrefying the biomass feedstock at a temperature below about 300°C, to produce a plurality of solid biomass particles having at least one of an increased brittleness and an increased susceptibility to catalytic conversion.

[0022] In various embodiments, the method includes agitating solid biomass particles, to reduce a size characterizing at least a portion of the particles. The method can also include separating a biomass-catalyst mixture comprising the particles and a catalyst into a fine fraction having particles of about a predetermined size and a coarse fraction having particles of greater than about the predetermined size. Separating can include using a high velocity cyclone.

[0023] In some embodiments, the refinery feedstock includes a hydrogen donor. The refinery feedstock can include a petrochemical feedstock. The refinery feedstock can include a product or a combination of products derived from crude oil and destined for further processing.

[0024] In certain embodiments, the refinery unit includes a petrochemical refinery unit.

[0025] In various embodiments, the method includes providing the biomass feedstock to the conventional refinery unit using a first feed system and providing the refinery feedstock to the conventional refinery unit using a second feed system.

[0026] In some embodiments, the refinery includes a first feed system providing the biomass feedstock to the conventional refinery unit and a second feed system providing the refinery feedstock to the conventional refinery unit.

[0027] In certain embodiments, the plurality of solid biomass particles are substantially characterized by individual sizes by individual sizes below about 1500 microns. The plurality of solid biomass particles can substantially characterized by at least about 80% (e.g., by weight) of the particles having individual sizes of about 1500 microns or less.

[0028] Other aspects and advantages of the invention will become apparent from the following drawings and description, all of which illustrate principles of the invention, by way of example only.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The advantages of the invention described above, together with further advantages, can be better understood by referring to the following description taken in conjunction with

the accompanying drawings. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention.

[0030] FIG. 1 illustrates a sectional view of an exemplary refinery unit for coprocessing a biomass feedstock and a refinery feedstock.

[0031] FIG. 2 illustrates a sectional view of an exemplary refinery unit for coprocessing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas.

DETAILED DESCRIPTION OF THE INVENTION

[0032] The invention relates to processing biomass with a hydrogen donor (e.g., refinery feedstock, hydrogen gas), for example, to convert biomass together with a hydrogen donor into a fuel, specialty chemical, or intermediate product. The invention includes refinery units for co-processing a biomass feedstock and a refinery feedstock (e.g., with or without the presence of hydrogen gas). The invention also includes methods for co-processing a biomass feedstock and a refinery feedstock (e.g., with or without the presence of hydrogen gas). Furthermore, the invention includes methods for providing (e.g., building, adapting, retrofitting, and the like) refinery units for coprocessing a biomass feedstock and a refinery feedstock (e.g., with or without the presence of hydrogen gas).

[0033] Operation of the refinery units and use of the methods can include transfer of hydrogen from the hydrogen source (e.g., refinery feedstock, hydrogen gas, or a combination thereof) to a feedstock (e.g., biomass feedstock). Accordingly, the invention provides a cost-effective alternative to conventional hydroprocessing (e.g., requiring high pressure and large amounts of hydrogen gas, and not amenable to continuous processing in a fluidized type reactor). The invention also provides methods and apparatus adapted specifically to co-processing a biomass feedstock and a refinery feedstock. Accordingly, the invention provides technical advantages (e.g., processing under mild conditions, product selectivity) and cost advantages (e.g., processing with lower cost equipment, conditions, reactants, and/or feedstock) over conventional petrochemical refinery units and methods (e.g., hydroprocessing).

[0034] Operation of the refinery units and use of the methods can also result in higher yield and higher value products being produced from both the biomass and refinery feedstock. For

example, biomass feedstock including cellulose tends to produce oxygenated acidic compounds and aromatics. Refinery feedstock including paraffins tends to produce low octane products having pour point problems. By co-processing, the biomass feedstock produces hydrocarbon products that are richer in hydrogen, contain less undesired oxygenic and acidic groups, and fewer undesired aromatic compounds. Likewise, by co-processing, the refinery feedstocks produce higher octane products (e.g. with more olefins) having less pour point problems. Accordingly, co-processing can have they synergistic effect of simultaneously or substantially simultaneously increasing the commercial value and utility of product streams from both feedstocks.

Solid Biomass Particles

[0035] In various embodiments, biomass includes materials of photosynthetic (e.g., plant) origin having cellulose, hemicellulose, and/or lignin. Biomass includes materials produced by photosynthetic conversion of carbon dioxide and water using solar energy.

In general, biomass including cellulose, hemicellulose, and/or lignin originates from land plants. Some aquatic plants include little or no lignin. However, the invention is applicable to any biomass including any amount of cellulose, hemicellulose, and/or lignin. Biomass sources include, but are not limited to, cereal grains (e.g., including corn), grasses, sugar cane, trees, and the like. Biomass sources also include by-products of agricultural or forestry activities, such as straw, chopped straw, cotton linters, corn husks, corn stalks, corn cobs, wood chips, saw dust, bagasse, sugar beet pulp, tree bark, grasses, and the like. Biomass sources also include aquatic sources such as algae and seaweed.

[0036] Biomass sources can be used without requiring chemical pre-processing (e.g., chemically altering the biomass). In various embodiments, biomass sources include (chemically) unrefined material of photosynthetic origin. Biomass sources can be subjected to a drying and/or a particle size reduction step. Such a drying and/or a particle size reduction step does not significantly change the relative composition of the biomass in terms of cellulose, hemicellulose and/or lignin and therefore such a step is not necessarily considered refining.

[0037] In various embodiments, biomass feedstock can include particles that are solid and in a finely divided form (e.g., saw dust and ground straw). Biomass feedstock can include solid

materials as well as materials that might be classified as liquids, but that have a very high viscosity (e.g., small or large colony algae). Biomass particles can be prepared from biomass sources and larger particles by techniques such as milling, grinding, pulverization, and the like. Conventional paper processing/pulping methods and equipment can be used to prepare biomass particles. For example, biomass from sources such as straw and wood can be converted to particles in a size range of about 5 mm to about 5 cm using techniques such as milling or grinding.

Pre-treating biomass

[0038] In various embodiments, biomass feedstock can be chemically and/or physically pre-treated. Examples of pretreatment steps in which recycled aqueous phase can be used include demineralization, heat treatment, and steam explosion.

[0039] Demineralization can include removing at least a fraction of a naturally occurring mineral from biomass (e.g., prior to a pyrolysis or catalytic cracking reaction). Demineralization can improve control over the reaction of the biomass. Many of the minerals naturally present in the biomass material can be catalytically active (e.g., potassium, iron). Although these materials can catalyze reactions, they can also increase coke yield, which is generally undesirable. Even when catalytic activity is desired, it can be preferable to first demineralize the biomass material so as to control the composition of their catalyst system.

[0040] One method of demineralization includes contacting biomass with an aqueous solvent and allowing the biomass material to swell. After swelling, at least part of the aqueous solvent can then be removed from the biomass by mechanical action (e.g., kneading, pressing). Swelling and dewatering steps can be repeated to control the amount of minerals that are removed from the biomass. In addition to removing minerals from the biomass, the swelling and dewatering steps can make the biomass material more susceptible to a subsequent reaction.

[0041] Although essentially any aqueous solvent can be used for demineralization, the aqueous phase of a liquid pyrolysis product can be particularly effective. The effectiveness is believed to be due to the presence of organic acids (e.g., carboxylic acid, acetic acid) in the aqueous phase. Without wishing to be bound by any theory, the acidity of the aqueous phase

can facilitate the mobilization of minerals in the biomass. For example, the chelating effects of carboxylic acids can contribute to the solubilization and removal of mineral cations.

[0042] Solvent explosion can include contacted the biomass with a pressurized solvent at a temperature above its natural boiling point (e.g., at atmospheric pressure). The pressurized solvent is in a liquid phase and swells the biomass. Then, the solvent is de-pressurized, causing rapid evaporation (i.e., boiling) of the solvent. This rapid evaporation can be referred to as solvent explosion. The solvent explosion can physically rupture the biomass material, thereby making it more accessible in a subsequent reaction.

[0043] Examples of solvents that can be used in solvent explosion include ammonia, carbon dioxide, water, and the like. If water is used as the solvent, the process can be referred to as steam explosion. It will be understood that the term steam explosion can be considered a misnomer, and that the term water explosion can be more accurate. Nevertheless, the term steam explosion will be used herein because it is an accepted term of art. The aqueous phase of the liquid pyrolysis product can be used in a steam explosion.

[0044] When steam explosion is combined with demineralization, the steam explosion can be carried out before or after the demineralization. For example, it can be advantageous to conduct the demineralization after the steam explosion because the steam explosion pretreatment can make the minerals more accessible, thereby making the demineralization more effective.

[0045] Heat treatment can include heating the biomass to a temperature of about 100-300°C in an oxygen-poor or oxygen-free atmosphere. The term oxygen-poor can refer to an atmosphere containing less oxygen than ambient air. The heat treatment can carried out in the presence of sufficient solvent (e.g., water) to swell the biomass material. The heat treatment can be carried out in a closed vessel to mitigate evaporation of the solvent. In some examples, the vapor (e.g., steam) formed under these conditions can displace oxygen present in the vessel and produce an oxygen-poor atmosphere. In one example, the aqueous phase of a liquid pyrolysis product can be the solvent in such a heat treatment.

[0046] Heat treatment can be carried out at a temperature low enough to mitigate carbon loss due to the formation of gaseous conversion products (e.g., CO, C02). A heat treatment can

use, for example, a temperature of about 100-200 °C. For example, a temperature can be about 100-140 °C. A heat treatment can have a duration, for example, of about 2 min to 2 hours. For example, a duration can be about 20-60 min. In various examples, pressure can be released at the end of a heat treatment by opening the heat treatment vessel, which can allows the heat treatment to be combined with a steam explosion pretreatment step.

[0047] Even where the heat treatment essentially does not produce any gaseous conversion products, it can still result in a modification of the biomass. For example, the heat treatment can make the biomass more brittle and more hydrophobic. Both effects can be desirable from the perspective of a subsequent reaction. For example, increased brittleness can facilitate girding the biomass to a small particle size, to increase reactivity in a pyrolysis reaction, and increased hydrophobicity can facilitate drying the biomass.

[0048] A heat pretreatment step can be combined with one or more additions pretreatment steps (e.g., demineralization, steam explosion). Because of the increased hydrophobicity of heat treated biomass, it can be preferable to conduct any demineralization and/or steam explosion steps prior to the heat treatment; with the exception that steam explosion can be combined with heat treatment as described above.

Agitation of Biomass Particles

[0049] In various embodiments, the method includes agitating solid biomass particles, to reduce a size characterizing at least a portion of the particles. In some embodiments, agitating is facilitated by fluid conveyance, including, without limitation, by gas flow or pneumatic conveyance. Agitating can be conducted in a vertical vessel, such as a riser or downer. An agitator can include a conveyor, a riser, or downer. A riser (up flow) or a downer (down flow) can be, for example, a hollow vertical vessel terminating in a larger diameter vessel, which houses high velocity (e.g., about 60-80 m/s or 18-24 m/s) cyclones that may or may not be physically connected to the riser termination point. The height of a riser or downer can be, for example, between about 15 ft (5 m) and about 60 ft (18 m) and the diameter can be, for example, between about 1 ft (0.3 m) and about 4 ft (1.2 m). Agitating can be facilitated by a gas (e.g., gas can convey the particles such that they are abraded or ground by other particles, catalyst, and/or inorganic particulate material). The gas can be one or more of air, steam, flue gas, carbon dioxide, carbon monoxide, hydrogen, and hydrocarbons, (e.g.

methane). The gas can be a gas having a reduced level of oxygen (compared to air) or can be substantially oxygen-free. In another embodiment, an agitator can be a mill (e.g., ball or hammer mill) or kneader or mixer (e.g., for mechanical, as opposed to pneumatic, agitation).

[0050] In certain embodiments, agitating includes causing the solid biomass particles to be conveyed at a velocity of greater than about 1 m/s. For example, the velocity can be measured relative to a vessel in which the particles are conveyed. Agitating can include causing the solid biomass particles to move at a velocity of greater than about 10 m/s. Agitating can include causing at least a portion of the solid biomass particles to move at a velocity of greater than about 100 m/s. An agitator can be adapted to cause the solid biomass particles to move at a velocity of greater than about 1 m/a, greater than about 10 m/s, and/or greater than about 100 m/s. Other velocities include velocities of greater than about 5, 25, 50, 75, 125, 150, 175, 200, 225, and 250 m/s.

[0051] For example, the velocity is selected from the group consisting of: between about 10 and about 20 m/s; between about 20 and about 30 m/s; between about 30 and about 40 m/s; between about 40 and about 50 m/s; between about 50 and about 60 m/s; between about 60 and about m/s; between about 70 and about 80 m/s; between about 80 and about 90 m/s; and between about 90 and about 100 m/s. The velocity can be about 10 m/s, about 20 m/s, about 30 m/s, about 40 m/s, about 50 m/s, about 60 m/s, about 70 m/s, about 80 m/s, about 90 m/s, or about 100 m/s. The velocity can be greater than about 10 m/s, about 20 m/s, about 30 m/s, about 40 m/s, about 50 m/s, about 60 m/s, about 70 m/s, about 80 m/s, about 90 m/s, or about 100 m/s.

[0052] In various embodiments, agitating solid biomass particles, to reduce a size characterizing at least a portion of the particles, is facilitated by agitating solid biomass particles together with a material that is harder than the biomass. For example, the material can be a catalyst or another inorganic particulate material. The amount of size reduction, and thus the size of the resulting solid biomass particles can be modulated by the duration of agitation and the velocity of agitation. Other factors such as the relative hardness of the catalyst or another inorganic particulate material, the dryness (e.g., brittleness) of the solid biomass particles, and the method/vessel(s) in which agitation occurs also modulate the amount of size reduction.

[0053] In embodiments using an abrading or grinding material that is a catalyst, the catalyst can become embedded in the biomass particles and/or the biomass particles can become embedded in the catalyst, which can facilitate catalytic conversion of the biomass. In such embodiments, agitating can facilitate formation of a mechano-chemical interaction between at least a portion of the catalyst and at least a portion of the solid biomass particles, which can facilitate catalytic conversion of the biomass.

[0054] Agitation can be carried out at an elevated temperature, for drying the biomass. An elevated temperature can be a temperature sufficient to dry the biomass, for example, between about 50 and about 150°C, or below about 200°C. Higher temperatures can be used, for example, where an agitating gas is oxygen-poor or substantially oxygen-free. Agitation can also be carried out at ambient temperature with dried biomass. Drying increases the hardness of the biomass particles, making the particles more susceptible to size reduction.

[0055] Agitation can be carried out by various different methods and in various different vessels. For example, in order of increasing abrasion, the agitation can be carried out in a fluid bed, a bubbling or ebullient bed, a spouting bed, or a conveyor. In one embodiment, agitation is carried out by fluid conveyance, including without limitation by gas flow or pneumatic conveyance. In one embodiment, agitation is carried out in a riser or a downer.

[0056] Agitating solid biomass particles, to reduce a size characterizing at least a portion of the particles, can result in a dispersion of particle sizes. For example, proper agitation the solid biomass particles as described above can result in individual particles sizes ranging from microns, to tens of microns, to tenths of centimeters, to centimeters or greater. The biomass can be subjected to a particle size reduction step, or can be collected in the form of particles (e.g., algae cells, colonies, flocculated algae, and the like).

[0057] In various embodiments, the biomass particles are reduced to, or have, an average particle size of less than about 1000 microns. Alternatively, the biomass particles are reduced to, or have, an average particle size of greater than about 1000 microns. The plurality of solid biomass particles can be substantially characterized by individual sizes below about 2000, 1900, 1800, 1700, 1600, 1500, 1400, 1300, 1200, 1100, 1000,900,800, 700, 600, 500, 400, 300, 200, or 100 microns. In various embodiments, at least a fraction of the biomass particles have a size of about 1-2000, 1-1500,1-1000, or 1000-2000 microns. For example, the biomass

particles can have an average size of less than about 2000, 1750, 1500, 1250, 1000, 750, 500, or 250 microns. In some embodiments, at least a fraction of the biomass particles are reduced to a size below about 500, 475,450, 425,400, 375,350, 325,300,275,250, 225,200,175,150, 125, 100, 90, 80, 70, 60, 50, 40, 30, 20, 15, 10, or 5 microns. Individual particles sizes can range from microns, to tens of microns, to tenths of centimeters, to centimeters or greater.

[0058] At least a fraction of the biomass particles can be reduced to a size between about 1 mm and 1 micron. For example, the biomass particles can have an average size of about 300-500 microns comprised of mainly individual sizes of about 10-1,000 microns. In various embodiments, the plurality of solid biomass particles are substantially characterized by an average size between about 50 and about 70 microns and individual sizes between about 5 and about 250 microns. In other embodiments, the plurality of solid biomass particles are substantially characterized by an average size between about 10 and about 20 microns and individual sizes between about 5 and about 50 microns. In other embodiments, the plurality of solid biomass particles are substantially characterized by an average size between about 100 and about 150 microns and individual sizes between about 5 and about 500 microns.

[0059] Solid biomass particles do not necessarily assume a spherical or spheroid shape. For example, solid biomass particles can be needle shaped and/or assume another cylinder-like or elongated shape. Accordingly, size does not necessarily correspond to a single diameter (although it could correspond to an average diameter or diameter in a singe, for example largest or smallest, dimension). In various embodiments, size can correspond to the mesh size or a screen size used in separation and/or sizing the solid biomass particles.

[0060] International Publication No. WO 2007/128798 Al by O'Connor, the disclosure of which is incorporated herein by reference in its entirety, discloses agitating solid biomass particles and catalysts. In particular, paragraphs [0027] to [0072] of WO 2007/128798 Al are incorporated herein by reference.

[0061] International Publication No. WO 2008/009643 A2 by O'Connor, the disclosure of which is incorporated herein by reference in its entirety, discloses agitating solid biomass particles and catalysts. In particular, paragraphs [0009] to [0051] of WO 2008/009643 A2 Al are incorporated herein by reference.

Separation of Biomass Particles

[0062] In various embodiments, methods include separating a biomass-catalyst mixture into a fine fraction and a coarse fraction. The biomass-catalyst mixture includes the biomass particles and a catalyst. The fine fraction includes particles of about a predetermined size. The coarse fraction includes particles of greater than about the predetermined size. Separating the mixture into a fine fraction and a coarse fraction can have several effects. For example, a fine fraction can be selected to include particles of about a predetermined size, below about a predetermined size, and/or within a predetermined size range. In some embodiments, the fine fraction can be selected to consist essentially of particles of about a predetermined size, below about a predetermined size, and/or within a predetermined size range. Furthermore, a coarse fraction can be recycled for further size reduction and/or to produce more of a fine fraction.

[0063] A predetermined size can be selected based upon one or more requirements of a subsequent reaction. For example, a predetermined size can be selected to facilitate substantial catalytic conversion of the fine fraction in a subsequent reaction. A predetermined size can be selected to facilitate contact, impregnation, and/or interaction of the catalyst and the biomass. In some embodiments, a predetermined size can be about 2000,1900,1800,1700,1600,1500,1400,1300,1200, 1100, 1000,900,800,700,600, 500,450,400,350,300,250,200, 150, 100,50,45,40,35,30,25,20, 15, 10,or 5 microns, or any individual value there between. In one embodiment, a predetermined size is about 15 microns. In one embodiment, a predetermined size is about 10 microns. A predetermined size can be between about 1 and 2000 microns or between about 5 and about 1000 microns.

[0064] Separating can be facilitated by a cyclonic action. A separator can include a single cyclone. Alternatively, a separator can include a plurality of cyclones arranged, for example, in parallel, series, as a third stage separator, or as a fourth stage separator. U.S. Patent No. 6,971,594 to Polifka, the disclosure of which is incorporated herein by reference in its entirety, discloses cyclonic action and cyclone separators that can be adapted and employed with the invention. In particular, FIG. 2, the text corresponding to FIG. 2, and the text corresponding to column 4, line 55 to column 11, line 55 of U.S. Patent No. 6,971,594 are incorporated herein by reference.

[0065] Separating can be achieved by other known methods. For example, separating can be achieved by screening, settling, clarification, and the like.

Catalysts and Inorganic Particulate Materials

[0066] A catalyst can be any material that facilitates the conversion of organic components of the biomass into fuels, specialty chemicals, or precursors thereof. In various embodiments, the catalyst includes a solid particulate catalyst and the biomass-catalyst mixture includes at least a portion of the catalyst mechano-chemically interacting with at least a portion of the solid biomass particles. In some embodiments, the catalyst includes a catalyst capable of being at least partly dissolved or suspended in a liquid and the biomass-catalyst mixture includes at least a portion of the catalyst impregnating at least a portion of the solid biomass particles. A catalyst can be or include a water-insoluble catalyst, a fluid catalytic cracking catalyst, and a petroleum coke catalyst.

[0067] In various embodiments, a catalyst is a particulate inorganic oxide. The particulate inorganic oxide can be a refractory oxide, clay, hydrotalcite, hydrotalcite-like material, clay, layered hydroxy salt, mixed metal oxide, a calcination product of any of these materials; or a mixture thereof. Suitable refractory inorganic oxides include alumina, silica, silica-alumina, titania, zirconia, and the like. In one embodiment, the refractory inorganic oxides have a high specific surface (e.g., a specific surface area as determined by the Brunauer Emmett Teller ("BET") method of at least 50 m2/g). Suitable clay materials include cationic and anionic clays, for example, smectite, bentonite, sepiolite, atapulgite, hydrotalcite, and the like. Suitable metal hydroxides and metal oxides include bauxite, gibbsite and their transition forms. Other suitable (and inexpensive) catalysts include lime, brine, and/or bauxite dissolved in a base (e.g., NaOH), or a natural clay dissolved in an acid or a base, or fine powder cement (e.g., from a kiln). Suitable hydrotalcites include hydrotalcite, mixed metal oxides and hydroxides having a hydrotalcite-like structure, and metal hydroxyl salts.

[0068] In some embodiments, a catalyst can be a catalytic metal. The catalytic metal can be used alone or together with another catalyst, refractory oxide, and/or binder. A catalytic metal can be used in a metallic, oxide, hydroxide, hydroxyl oxide, or salt form, or as a metallo-organic compound, or as a material including a rare earth metal (e.g., bastnesite). In certain embodiments, the catalytic metal is a transition metal. The catalytic metal can be a non-noble

transition metal. For example, the catalytic metal can be iron, zinc, copper, nickel, and manganese. In one embodiment, the catalytic metal is Iron.

[0069] A catalytic metal can be contacted with the biomass by various methods. In one embodiment, the catalyst is added in its metallic form, in the form of small particles. Alternatively, the catalyst can be added in the form of an oxide, hydroxide, or a salt. In another embodiment, a water-soluble salt of the metal is mixed with the biomass and the inert particulate inorganic material to form an aqueous slurry. The biomass and the aqueous solution of the metal salt can be mixed before adding the inert particulate inorganic material to facilitate the metal's impregnating the biomass. The biomass can also be mixed with the inert particulate inorganic material prior to adding the aqueous solution of the metal salt. In still another embodiment, an aqueous solution of a metal salt is mixed with the inert inorganic material, the material is dried prior to mixing it with the particulate biomass, and the inert inorganic material is thus converted to a heterogeneous catalyst.

[0070] The biomass-catalyst mixture can include an inorganic particulate material. An inorganic particulate material can be inert or catalytic. An inorganic material can be present in a crystalline or quasi- crystalline form. Exemplary inert materials include inorganic salts such as the salts of alkali and alkaline earth metals. Although these materials do not necessarily contribute to a subsequent chemical conversion of the polymeric material, it is believed that the formation of discrete particles of these materials within the biomass can work as a wedge to mechanically break up or open the structure of the biomass, which can increase the biomass surface accessible to microorganisms and/or catalysts. In one embodiment, the breaking up or opening is facilitated by crystalline or quasi-crystalline particles.

[0071] Inorganic particulate material can have catalytic properties. For example, a catalytic inorganic particulate material can be a metal oxide or hydroxide such as an alumina, silica, silica aluminas, clay, zeolite, ionic clay, cationic layered material, layered double hydroxide, smectite, saponite, sepiolite, metal hydroxyl salt, and the like. Carbonates and hydroxides of alkali metals, and the oxides, hydroxides and carbonates of alkaline earth metals can also have catalytic properties. Inorganic particulate material can include mixtures of inorganic materials. Inorganic particulate material can include a spent (resid) fluid catalytic cracking

catalyst containing (thermally treated) layered material. Employing spent catalyst can involve reusing waste material. The spent catalyst can be ground of pulverized into smaller particles to increase its dispersibility. Inorganic particulate material can also include sandblasting grit. Employing sandblasting grit can involve reusing waste material, which can include particles of iron, and lesser quantities of other suitable metals such as nickel, zinc, chromium, manganese, and the like (e.g., grit from steel sandblasting).

[0072] Contacting the catalyst, and optionally the inorganic particulate material, with the biomass, can be achieved by various methods. One method includes heating and fluidizing a mixture of the particulate biomass material and the inert inorganic material, and adding the catalyst to the mixture as fine solid particles. Another method includes dispersing the catalytic material in a solvent (e.g., water), and adding the solvent to the mixture of particulate biomass material and the inert inorganic material.

[0073] European Patent Application No. EP 1 852466 A1 by O'Connor, the disclosure of which is incorporated herein by reference in its entirety, discloses catalysts and contacting catalysts and biomass. In particular, paragraphs [0011] to [0043] of EP 1 852466 A1 are incorporated herein by reference.

[0074] International Publication No. WO 2007/128799 A1 by O'Connor, the disclosure of which is incorporated herein by reference in its entirety, discloses catalysts and contacting catalysts and biomass. In particular, paragraphs [0015] to [0054] of WO20071128799 A1 are incorporated herein by reference.

Removing Metals and/or Minerals

[0075] In various embodiments, a pretreatment can reduce an ash content of biomass, or a hazardous disposal characteristic of an ash that can be subsequently produced. Removal of minerals (e.g., ash precursors) from the biomass can reduce the ash content. Removal of metals (e.g., ash precursors), particularly heavy metals, can also reduce ash content and prevent metal contamination of waste products, thereby facilitating disposal of waste by providing an uncontaminated waste product and reducing the cost of disposing of the waste product.

[0076] A pretreatment for reducing ash content can include swelling the biomass with a solvent and then removing solvent from the swollen biomass material by applying mechanical action to the biomass material. Ash precursors, such as dissolved minerals and/or metals, will thus be removed with the solvent. The solvent can be aqueous. The solvent can include an acid or base (e.g., inorganic acid or base). The mechanical action can occur in an agitator and/or a kneader. The mechanical action can be exerted by equipment such as a high shear mixer, kneader, colloid mill, planetary mixer, mix-miller, or ball mill. A pretreatment for reducing ash content can include washing or slurrying with an aqueous phase having pH above or below neutral, ion exchange (e.g., with ammonium solutions that would exchange a hydrogen ion with a metal ion), and steam stripping are possible methods.

[0077] Pretreatment can reduce ash content to less than about 10 wt%, 9 wt%, 8 wt%, 7 wt%, 6 wt%, 5 wt%, 4 wt%, 3 wt%, 2 wt%, or 1 wt%, based on dry weight of the biomass material. The pretreatment can reduce metal (e.g., Fe) content to less than about 3,000, 2,500, 2,000, 1,500, 1,000, or 500 mg/kg, based on dry weight of the biomass.

Kneaders

[0078] A kneader can be used to knead the solid biomass particles and the catalyst, to make at least a portion of the solid biomass particles accessible to at least a portion of the catalyst. The kneader can be an extruder, miller, mixer, or grinder. The kneader can operate at greater than ambient temperature, for example, to facilitate removal or water and/or other solvent. For example, the kneader can be heated and/or heated gas (e.g., steam) can be provided to heat the biomass and catalyst.

[0079] In various embodiments, the kneader employs a solvent. The solvent can be water, an alcohol (e.g., ethanol or glycerol), a bio-oil or another product from the conversion of the biomass, a liquid acid, an aqueous solution of an acid or base, liquid CO2, and the like. In one embodiment, the solvent is water (e.g., added water and/or water inherently present in the biomass), which can be selected for its availability, low cost, and/or ease of handling. In another embodiment, the solvent is a liquid produced during the subsequent conversion of the biomass, which can be selected for its availability. A solvent can be selected to improve penetration of a catalyst into biomass.

A solvent can also improve penetration of a catalyst into biomass because a dry biomass can be more difficult to penetrate. A solvent can also be selected to remove ash precursors. Solvents can be removed (e.g., by drying) prior to subsequent processing and/or conversion. A kneader can remove at least a portion of a solvent absorbed in a biomass (e.g., by mechanical action and draining). Embodiments employing a kneader and a solvent can reduce the ash and/or mineral and/or metal content of the biomass.

[0080] In various embodiments, the biomass can be kneaded with one or more solid catalyst and/or inorganic particulate material. In some embodiments, the biomass can be kneaded with a dissolved and/or suspended catalyst. The dissolved and/or suspended catalyst can be used together with one or more solid catalyst and/or inorganic particulate material. Kneading can be continued and/or repeated to produce a biomass-catalyst mixture having the desired properties (e.g., particle size and/or degree of sensitization).

[0081] International Publication No. WO 20071128800 Al by O'Connor, the disclosure of which is incorporated herein by reference in its entirety, discloses catalysts and sensitizing biomass, as well as sensitizing by kneading. In particular, paragraphs [0025] to [0074] with respect to catalysts and sensitizing biomass, as well paragraphs

[0076] to [0086] with respect to sensitizing by kneading, of WO 20071128800 Al are incorporated herein by reference.

Disintegrators

[0082] The disintegrator processes plant matter at a location in close proximity to an agricultural site used to produce such plant matter, to produce the solid biomass particles. In operation, a disintegrator can be used to modify the consistency of, e.g., biomass feedstock, and/or to reduce its average particle size. The disintegrator can include at least one of a mill, fragmenter, fractionator, granulator, pulverizer, chipper, chopper, grinder, shredder, mincer, and a crusher. Apparatuses including a disintegrator can process plant matter at a location in close proximity to an agricultural site used to produce such plant matter, to produce the solid biomass particles. U.S. Patent No. 6,485,774 to Bransby, the disclosure of which is incorporated herein by reference in its entirety, discloses a method of preparing and handling

chopped plant materials. In particular, the text corresponding to column 1, line 45 to column 4, line 65 of U.S. Patent No. 6,485,774 is incorporated herein by reference.

Examples

[0083] Examples 1 and 2, FIGS. 1 and 2, and the description below illustrate exemplary methods and apparatuses for co-processing a biomass feedstock and a refinery feedstock. Catalyst, reaction vessel(s), pretreatment, treatment, and reaction conditions can each be selected based upon the type of biomass and the desired product(s). The methods can be part of a broader method (e.g., a broader method can include anyone or more steps of harvesting biomass, pre-processing biomass, further processing, refining, upgrading, separating, transporting products, intermediates, and the like).

[0084] In various embodiments, the intermediates include hydrocarbons from which oxygen can be stripped (e.g., as CO, CO2, H_20) to produce traditional fuel or specialty chemical products such as light gases, naphtha, heating oils, jet fuel, and the like. In general, processing proceeds by cracking and deoxygenating (as necessary) polymeric compounds in the biomass into a fuel or specialty chemical product. In various embodiments, intermediates can be stripped quickly from the catalysts and unconverted biomass to limit secondary (e.g., undesired) reactions.

[0085] The apparatuses can be part of a larger apparatus. For example, a larger apparatus can include one or more systems for harvesting, pretreating, further processing, refining, upgrading, separation, transportation, and the like. The invention can be carried out at a site adjacent to a biomass growth source. For example, the site can be near a source of a biomass feedstock, which can reduce transportation costs for a biomass feedstock and a liquid product. Operation at a site adjacent to a biomass growth source can also include other advantages such a recycling water and ash byproducts to the biomass growth source.

[0086] A system can include a first feed system and a second feed system, to facilitate co-process a liquid feedstock and a solid feedstock, or a biomass feedstock and a refinery/petroleum feedstock. The first feed system can provide the liquid feedstock to the refinery unit and the second feed system can provide the solid feedstock to the refinery unit. In embodiments where a biomass feedstock is co-processed with a refinery/petroleum

feedstock, the first feed system can provide the biomass feedstock to the refinery unit and the second feed system can provide the refinery/petroleum feedstock to the refinery unit. The first feed system can also be adapted to provide a suspension of a solid biomass feedstock in a liquefied biomass feedstock or a refinery/petroleum feedstock (e.g., torrefied biomass particles suspended in a biocrude or crude oil). A system can include a third feed system that can provide hydrogen gas to the refinery unit.

[0087] Example I: A biomass feedstock and a refinery feedstock can be coprocessed in a refinery unit. A liquid product can be produced by catalytically cracking a biomass feedstock and a refinery feedstock in a refinery unit having a fluidized reactor. Catalytically cracking includes transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock.

[0088] Example 2: A biomass feedstock and a refinery feedstock can be coprocessed in the presence of hydrogen gas in a refinery unit. A liquid product can be produced by hydrocracking or hydrotreating a biomass feedstock and a refinery feedstock in the presence of hydrogen gas in a refinery unit having a hydrocracking or hydrotreating reactor. Hydrocracking or hydrotreating includes transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock.

[0089] In these and other examples, a biomass feedstock can include a plurality of solid biomass particles. A plurality of solid biomass particles can be characterized by an average size between about 50 and about 750 microns and individual sizes between about 0.1 and about 1000 microns. The plurality of solid biomass particles can be substantially characterized by at least about 80% of the particles having individual sizes of about 10 (or 15 or 20) microns or less. A method can include agitating solid biomass particles, to reduce a size characterizing at least a portion of the particles. A method can also include separating (e.g., with a high velocity cyclone) a biomass-catalyst mixture including the particles and a catalyst into a fine fraction having particles of about a predetermined size and a coarse fraction having particles of greater than about the predetermined size.

[0090] The biomass feedstock can include a catalyst (e.g., a basic catalyst, a zeolite catalyst). In certain examples, the catalyst can be one or more of a hydrotreating, hydrocracking, NiMo, CoMo, NiCoMo, and noble metal catalyst. The catalyst can be in mechano-chemical

interaction with at least a portion of the plurality of solid biomass particles. For example, the biomass feedstock can be a plurality of lignocellulosic biomass particles in mechano-chemical interaction with a basic catalyst. The biomass feedstock can include an inorganic particulate material. In some cases, a biomass feedstock can include a deoxygenated liquid product of pyrolysis or catalytic cracking, a bio-oil, or fraction of the liquid product or bio-oil. A biomass feedstock can include plant oil or waste oil (e.g., used fat from a food source such as used restaurant frying oil). The biomass feedstock can include a heavy liquid fraction of a liquefied biomass feedstock. The biomass feedstock can be substantially free of a mineral component (e.g., contamination) capable of inactivating a catalyst.

[0091] Solid biomass particles can be pre-processed (e.g., chemically and/or physically). For example, the solid biomass particles can be dried and/or subjected to particle size reduction. Pre-processing can increase brittleness, susceptibility to catalytic conversion (e.g., by roasting, toasting, and/or torrefication, for example, at a temperature below about 300,375,350,325,300,275,250,225,200, 175, 150, 125, or 100°C) and/or susceptibility to mixing with a petrochemical feedstock (e.g., by increasing hydrophobicity). Pre-processing can include de-mineralizing the biomass feedstock (e.g., removing ash precursors from the solid biomass particles, removing a mineral component capable of inactivating a catalyst).

[0092] In these and other examples, a refinery feedstock can be a product or a combination of products derived from oil (e.g., crude oil, petroleum product, or more generally any fossil fuel or fossil fuel precursor). Petroleum products are obtained from the processing of crude oil, natural gas, and other hydrocarbon compounds. Petroleum products include unfinished oils, liquefied petroleum gases, pentanes plus, aviation gasoline, motor gasoline, naphtha-type jet fuel, kerosene-type jet fuel, kerosene, distillate fuel oil, residual fuel oil, petrochemical feedstocks, special naphthas, lubricants, waxes, petroleum coke, asphalt, road oil, still gas, and the like.

[0093] A refinery feedstock can include a hydrogen donor (e.g., capable of transferring hydrogen to carbon and oxygen from the biomass feedstock). A refinery feedstock can be transformed into one or more components and/or finished products and can be destined for further processing other than blending. For example the refinery feedstock can include one or more of an atmospheric gas oil or a vacuum gas oil from a paraffinic or naphthenic crude

source, a resid from a paraffinic or naphthenic crude source, a hydrotreated vacuum gas oil, a hydrotreated resid, and a hydrotreated light cycle oil. Naphthenic feedstocks can be an effective hydrogen source because they hydrogen atoms are readily separated from the component napthenes. The refinery feedstock can include a petrochemical feedstock. A petrochemical feedstock can be essentially any petroleum or petroleum distillate that can function as a hydrogen source or hydrogen donor.

[0094] In certain example, hydrogen gas can be present at an elevated pressure (e.g., using conventional hydroprocessing parameters) or at a lowered pressure (e.g., at about, or slightly above, atmospheric pressure). They reaction atmosphere can be essentially hydrogen gas, hydrogen gas and an inert gas (e.g., nitrogen), or hydrogen and a process gas (e.g., steam, CO2).

[0095] In these and other examples, a refinery unit can include a reactor (e.g., fluidized reactor) that can support catalytic cracking of the biomass feedstock that includes transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock. The catalytic cracking can convert the biomass into hydrocarbon compounds (including carbon from the biomass) and water (including oxygen from the biomass). Hydrocarbon compounds can include oxygenated hydrocarbons like aldehydes, alcohols, ketones, and acids (e.g., for use a specialty chemicals) as well as straight chain or branched alkynes, alkenes, and alkynes. CO and CO2 (including both carbon and oxygen from the biomass) can also be produced. Liquid (e.g., hydrocarbon) product yield can be increased, controlled, optimized, and/or maximized by increasing H20 formation relative to at least one of CO and CO2 formation.

[0096] The methods can employ a reaction time that favors kinetic products relative to equilibrium products. A reaction time can be about 2 seconds or less (e.g., about 2. 1.75, 1.5, 1.25, 1,0.9,0.8,0.7,0.6,0.5,0.4,0.3,0.2,0.1 seconds). A reaction temperature can be in a range of about 200-1000 0c. For example, the reaction temperature can be about 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475, 500,525,550,575,600,625,650,675,700,725, 750, 775,800,825,850,875,900,925, 950,975, or 1000 °C. The reaction temperature can be in a range of about 200-1,000, 300-900, 300-850, 400-800, 400-750, 450-700, 450-650, 450-600, 500-600, and 500-550

[0097] A refinery unit can be a conventional petrochemical refinery unit, for example, a fluid catalytic cracking (FCC) unit. The FCC unit can be modified or adapted (e.g., retrofitted equipment and/or altered operating parameters) for co-processing a biomass feedstock and a petrochemical feedstock. Alternatively, a refinery unit can be designed and purpose-built (e.g., employing petrochemical refinery unit hardware and operating parameters).

[0098] The refinery unit can include a fluid bed reactor. A fluid bed reactor can support high throughput processing (e.g., a traditional hydro treater reactor can require about 1 hour to accomplish what a fluid bed reactor can accomplish in about 1 second, due to differences in batch versus continuous operation and other operating conditions). A refinery unit can include a bed (e.g., fixed bed and/or ebulating bed) reactor. A refinery unit can include a transport and/or riser reactor. Catalytic cracking reactors can include a system for refreshing, replacing, regenerating, and/or circulating catalyst.

[0099] The refinery unit can include a system for feeding a feedstock to a reactor. For example, the system can feed a refinery feedstock to the reactor. The system can feed a biomass feedstock (e.g., particles, fluidized particles, oil or other liquid) to the reactor. The system can feed two or more feedstocks to the reactor, such that the feedstocks mix in the reactor. Alternatively, the system can feed a pre-mixed feedstock to the reactor. The system can mix a refinery feedstock and a biomass feedstock, and feed the mixture to the reactor. In various embodiments, the system can control one or more operating parameters (e.g., heating of the individual and mixed feedstocks, flow volume, flow rate, flow timing, total amounts of feedstocks, and the like).

[0100] A refinery unit can also include anyone or more additional reaction vessels, knock out drums, strippers, towers, catalyst regenerators, catalyst coolers, and the like. A refinery unit can include a system for pre-processing the biomass feedstock. A refinery unit can include a system for providing biomass feedstock and petrochemical feedstock to a reaction vessel. A refinery unit can also include a system for transporting and/or storing a product (e.g., the liquid product or a fraction thereof).

[0101] A reactor can operate in either a continuous or switching (e.g., swing reactor) fashion. For example, each train of the refinery unit (e.g., hydroprocessing, hydrocracking unit) can be preceded by a pair of switchable guard reactors, so that catalyst in the reactor not in operation

can be replaced to remove contaminants without allowing a disruptive pressure drop to occur. A guard reactor can include a system for removing and replacing spent catalyst with fresh catalyst (e.g., an ebulating bed reactor with a system to remove spent catalyst and a system to add fresh catalyst). Where the reactor is operated in a continuous fashion, the catalyst can be continuously replaced or regenerated. A guard reactor can help extend catalyst life in the main reactor, by limiting catalyst deactivation due to contaminants substantially to the guard reactor.

[0102] In some cases, selecting a biomass feedstock having a relatively low mineral content (e.g., essentially cellulose) or de-mineralizing the biomass feedstock (e.g., by preprocessing) can mitigate the need to replace or regenerate the catalyst. Where the reactor is operated in a switching fashion, it can be important to limit the mineral content of the biomass feedstock to ensure sufficient catalytic activity throughout a reaction cycle. A guard reaction can also be employed to mitigate inactivation of the hydro treating catalyst by minerals in the biomass feedstock. Catalyst (e.g., in a guard reactor) can be selected to have a greater than average macroporous region pore volume, so that it can tolerate a greater quantity of contaminants before becoming inactivated. To some degree, sufficient catalytic activity can be ensured by selecting more active catalyst or providing more catalyst.

[0103] In these and other examples, a liquid product, or a fraction thereof, can be used or sold as a final product and/or can be subject to further processing/upgrading to producing a fuel or specialty chemical. Examples of fuels include light gases (ethane, propane, butane), naphtha, and distillates Get fuel, diesel, heating oil). Examples of chemicals include light olefins (ethylene, propylene, butylenes), acids (like formic and acetic), aldehydes, alcohols (ethanol, propanol, butanol, phenols), ketones, furans, and the like. In general, a liquid product, or a fraction thereof, is chemically similar or essentially indistinguishable (e.g., in terms of commercial use and/or commercial value) from a convention petrochemical product or intermediate.

[0104] FIG. 1 illustrates a sectional view of an exemplary refinery unit 100 for coprocessing a biomass feedstock and a refinery feedstock. The refinery unit 100 includes a fluidized reactor 105, a first system 110, and a second system 115. The first system 110 can provide a biomass feedstock and a refinery feedstock to the fluidized reactor. The second system 115

can refresh and/or regenerate a catalyst for the fluidized reactor 105. The first system 110 and the second system 115 support catalytic cracking including transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock within the fluidized reactor 105.

[0105] The invention also includes a method for providing a refinery unit (e.g., refinery unit 100) for co-processing a biomass feedstock and a refinery feedstock. The method includes providing a fluidized reactor (e.g., fluidized reactor 105). The method also includes providing a first system (e.g., first system 110) providing a biomass feedstock and a refinery feedstock to the fluidized reactor. Furthermore, the method includes providing a second system (e.g., second system 115) for at least one of refreshing and regenerating a catalyst in the fluidized reactor. The first system and the second system can support catalytic cracking that includes transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock within the fluidized reactor.

[0106] FIG. 2 illustrates a sectional view of an exemplary refinery unit 200 for coprocessing a biomass feedstock and a refinery feedstock in the presence of hydrogen. The refinery unit 200 includes a hydrocracking or hydrotreating reactor 205, a first system 210, and a second system 215. The first system 210 can provide a biomass feedstock, a refinery feedstock, and hydrogen gas to the hydrocracking or hydrotreating reactor 205. The second system 215 for at least one of refreshing and regenerating a catalyst in the hydrocracking or hydrotreating reactor 205. The first system 210 and the second system 215 support hydro cracking or hydrotreating including transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock in the hydro cracking or hydrotreating reactor 205.

[0107] The invention also includes a method for providing a refinery unit (e.g., refinery unit 200) for co-processing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas. The method includes providing a hydro cracking or hydrotreating reactor (e.g., hydrocracking or hydrotreating reactor 205). The method also includes providing a first system (e.g., first system 210) providing a biomass feedstock, a refinery feedstock, and hydrogen gas to the hydrocracking or hydrotreating reactor.

Furthermore, the method includes providing a second system (e.g., second system 215) for at least one of refreshing and regenerating a catalyst in the hydrocracking or hydrotreating reactor. The first system and the second system support hydrocracking or hydrotreating that includes transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock in the hydrocracking or hydrotreating reactor.

[0108] The refinery units 100, 200 can be used, for example, to execute methods like the method described in Example 1 and Example 2, respectively. Accordingly, the refinery units 100, 200 can include anyone or more of the elements, feedstocks, reactions, and product described in connection with Example 1 and Example 2.

[0109] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail can be made without departing from the spirit and scope of the invention as defined by the appended claims.

CLAIMS

1. A method for co-processing a biomass feedstock and a refinery feedstock in a refinery unit comprising:

producing a liquid product by catalytically cracking a biomass feedstock and a refinery feedstock in a refinery unit comprising a fluidized reactor,

wherein catalytically cracking comprises transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock.

2. A method for co-processing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas in a refinery unit comprising:

producing a liquid product by hydrocracking or hydrotreating a biomass feedstock and a refinery feedstock in the presence of hydrogen gas in a refinery unit comprising a hydrocracking or hydrotreating reactor,

wherein hydro cracking or hydrotreating comprises transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock.

3. The method of claim 1 or 2, further comprising increasing liquid product yield by increasing H_20 formation relative to at least one of CO and CO2 formation.
4. The method of claim 1 or 2, further comprising operating the refinery unit at a site adjacent to a solid biomass growth source.
5. The method of claim 1 or 2, wherein the biomass feedstock comprises a plurality of solid biomass particles.
6. The method of claim 5, wherein the plurality of solid biomass particles are substantially characterized by an average size between about 50 and about 1,000 microns and individual sizes between about 0.1 and about 1,500 microns.
7. The method of claim 5, further comprising a catalyst is in mechano-chemical interaction with at least a portion of the solid biomass particles.
8. The method of claim 1 or 2, wherein the biomass feedstock comprises a heavy liquid fraction of a liquefied biomass feedstock.

9. The method of claim 1 or 2, wherein the biomass feedstock is substantially free of mineral contamination capable of inactivating a catalyst.

10. The method of claim 1 or 2, wherein the refinery unit comprises a system for at least one of refreshing and regenerating a catalyst.

11. The method of claim 1 or 2, wherein the refinery feedstock comprises one or more of an atmospheric gas oil or a vacuum gas oil from a paraffinic or naphthenic crude source, a resid from a paraffinic or naphthenic crude source, a hydrotreated vacuum gas oil, a hydro treated resid, and a hydro treated light cycle oil.

12. A refinery unit for co-processing a biomass feedstock and a refinery feedstock comprising:

a fluidized reactor;

a first system providing a biomass feedstock and a refinery feedstock to the fluidized reactor; and

a second system for at least one of refreshing and regenerating a catalyst for the fluidized reactor,

wherein the first system and the second system support catalytic cracking comprising transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock within the fluidized reactor.

13. A method for providing a refinery unit for co-processing a biomass feedstock and a refinery feedstock comprising:

providing a fluidized reactor;

providing a first system providing a biomass feedstock and a refinery feedstock to the fluidized reactor; and

providing a second system for at least one of refreshing and regenerating a catalyst in the fluidized reactor,

wherein the first system and the second system support catalytic cracking comprising transferring hydrogen from the refinery feedstock to carbon and oxygen from the biomass feedstock within the fluidized reactor.

14. A refinery unit for co-processing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas comprising:

a hydrocracking or hydrotreating reactor;

a first system providing a biomass feedstock, a refinery feedstock, and hydrogen gas to the hydrocracking or hydrotreating reactor; and

a second system for at least one of refreshing and regenerating a catalyst in the hydrocracking or hydrotreating reactor,

wherein the first system and the second system support hydrocracking or

hydrotreating comprising transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock in the hydrocracking or hydrotreating reactor.

15. A method for providing a refinery unit for co-processing a biomass feedstock and a refinery feedstock in the presence of hydrogen gas comprising:

providing a hydrocracking or hydrotreating reactor;

providing a first system providing a biomass feedstock, a refinery feedstock, and hydrogen gas to the hydrocracking or hydrotreating reactor; and

providing a second system for at least one of refreshing and regenerating a catalyst in the hydrocracking or hydrotreating reactor,

wherein the first system and the second system support hydrocracking or hydrotreating comprising transferring hydrogen from the hydrogen gas to carbon and oxygen from the biomass feedstock and to carbon from the refinery feedstock in the hydrocracking or hydrotreating reactor.

16. The method of claim 1 or 2, further comprising using a basic catalyst.

17. The method of claim 1 or 2, further comprising using a zeolite catalyst.

18. The method of claim 1 or 2, wherein the reactor comprises a bed reactor.

19. The method of claim 1 or 2, wherein the reactor comprises a transport reactor.

20. The method of claim 1 or 2, wherein the reactor comprises at least one of a riser reactor and a downer reactor.

21. The method of claim 1 or 2, further comprising a reaction time of about 2 seconds or less.

22. The method of claim 1 or 2, further comprising a reaction time that favors kinetic products relative to equilibrium products.

23. The method of claim 1 or 2, further comprising de-mineralizing the biomass feedstock.

24. The method of claim 1 or 2, further comprising torrefying the biomass feedstock at a temperature below about 300°C, to produce a plurality of solid biomass particles having at least one of an increased brittleness and an increased susceptibility to catalytic conversion.

25. The method of claim 1 or 2, further comprising:

agitating solid biomass particles, to reduce a size characterizing at least a portion of the particles; and

separating a biomass-catalyst mixture comprising the particles and a catalyst into a fine fraction comprising particles of about a predetermined size and a coarse fraction comprising particles of greater than about the predetermined size.

26. The method of claim 24, wherein separating includes using a high velocity cyclone.

27. The method of claim 5, wherein the plurality of solid biomass particles are substantially characterized by at least about 80% of the particles having individual sizes of about 10 microns or less.

28. The method of claim 1 or 2, wherein the refinery feedstock comprises a hydrogen donor.

29. The method of claim 1 or 2, wherein the refinery unit comprises a petrochemical refinery unit.

30. The method of claim 1 or 2, wherein the refinery feedstock comprises a petrochemical feedstock.

31. The method of claim 1 or 2, further comprising using one or more of a hydrotreating, hydrocracking, hydrogenation, NiMo, CoMo, NiCoMo, noble metal, and supported noble metal catalyst.

32. The method of claim 1 or 2, wherein the refinery feedstock comprises a product or a combination of products derived from crude oil and destined for further processing.

33. The method of claim 1 or 2, further comprising:

providing the biomass feedstock to the conventional refinery unit using a first feed system; and

providing the refinery feedstock to the conventional refinery unit using a second feed system.

34. The refinery unit of claim 12 or 14, further comprising:

a first feed system providing the biomass feedstock to the conventional refinery unit; and a second feed system providing the refinery feedstock to the conventional refinery unit.

35. The method of claim 5, wherein the plurality of solid biomass particles are substantially characterized by individual sizes by individual sizes below about 1500 microns.

36. The method of claim 5, wherein the plurality of solid biomass particles are substantially characterized by at least about 80% of the particles having individual sizes of about 1500 microns or less.

37. The method of claim 1 or 2, further comprising using a water-insoluble catalyst.

38. The method of claim 1 or 2, further comprising using a solid base catalyst comprising hydrotalcite; hydrotalcite-like material; clay; layered hydroxy salt; mixed metal oxide; a calcination product of any of these materials; or a mixture thereof.

39. The method of claim 1 or 2, further comprising using an alumina catalyst.

40. The method of claim 1 or 2, further comprising using a fluid catalytic cracking catalyst.

41. The method of claim 1 or 2, further comprising using a petroleum coke catalyst.

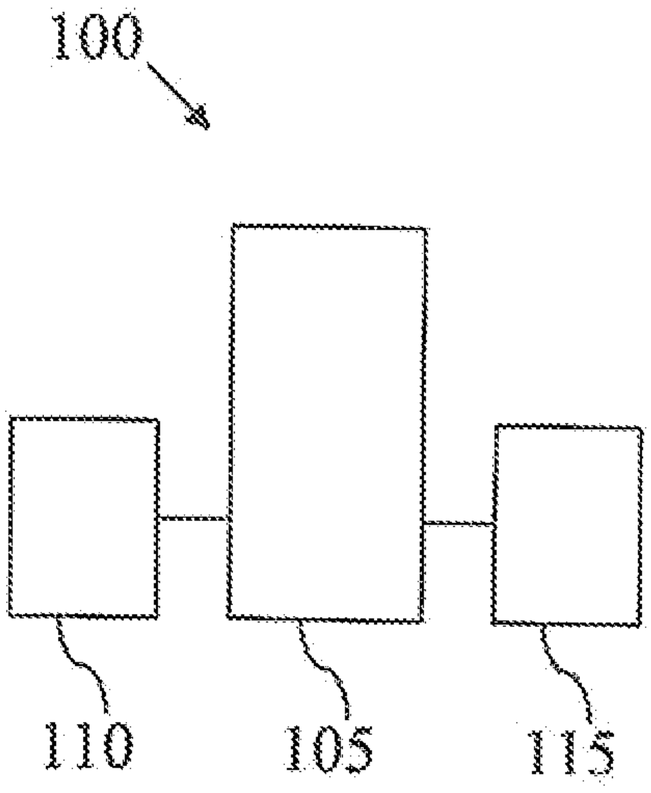


FIG. 1

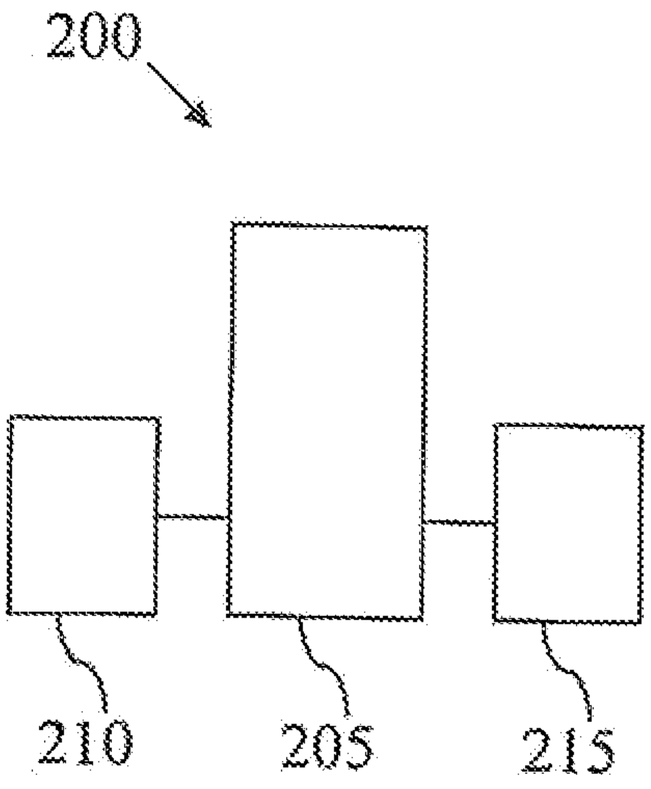


FIG. 2