



- (51) **International Patent Classification:** Not classified
- (21) **International Application Number:**
PCT/US2013/076325
- (22) **International Filing Date:**
19 December 2013 (19.12.2013)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/739,354 19 December 2012 (19.12.2012) US
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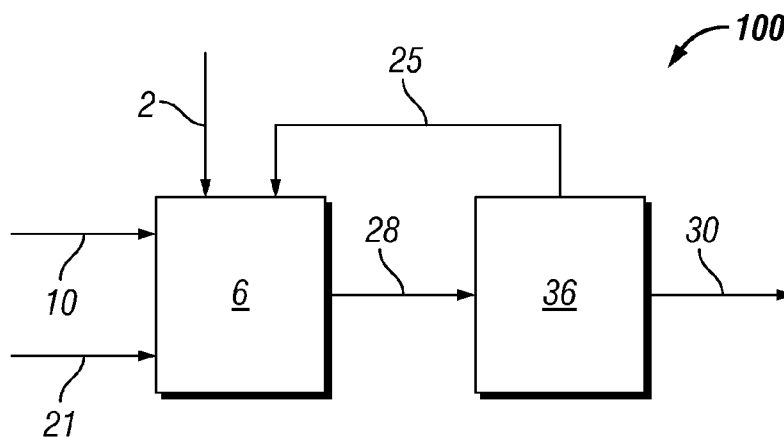
(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:

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

(54) **Title:** RECYCLABLE BUFFER FOR THE HYDROTHERMAL HYDROCATALYTIC TREATMENT OF BIOMASS

**FIG. 1**

(57) **Abstract:** A method of hydrothermal hydrocatalytic treating biomass is provided. Lignocellulosic biomass solids is provided to a hydrothermal digestion unit in the presence of a digestive solvent, at least one of ammonia or a source of ammonia, and a supported hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support. The lignocellulosic biomass solids and digestive solvent are heated in the presence of hydrogen, supported hydrogenolysis catalyst and the at least one of ammonia or a source of ammonia forming a product solution containing plurality of oxygenated hydrocarbons and ammonia. At least a portion of ammonia is separated and recycled to the hydrothermal digestion unit.

RECYCLABLE BUFFER FOR THE HYDROTHERMAL HYDROCATALYTIC TREATMENT OF BIOMASS

The present application claims the benefit of pending U.S. Provisional Patent
5 Application Serial No. 61/739354, filed December 19, 2012.

Field of the Invention

The invention relates to the hydrothermal hydrocatalytic treatment of biomass in
the production of higher hydrocarbons suitable for use in transportation fuels and industrial
chemicals from biomass.

10 Background of the Invention

A significant amount of attention has been placed on developing new technologies
for providing energy from resources other than fossil fuels. Biomass is a resource that
shows promise as a fossil fuel alternative. As opposed to fossil fuel, biomass is also
renewable.

15 Biomass may be useful as a source of renewable fuels. One type of biomass is
plant biomass. Plant biomass is the most abundant source of carbohydrate in the world due
to the lignocellulosic materials composing the cell walls in higher plants. Plant cell walls
are divided into two sections, primary cell walls and secondary cell walls. The primary
cell wall provides structure for expanding cells and is composed of three major
20 polysaccharides (cellulose, pectin, and hemicellulose) and one group of glycoproteins. The
secondary cell wall, which is produced after the cell has finished growing, also contains
polysaccharides and is strengthened through polymeric lignin covalently cross-linked to
hemicellulose. Hemicellulose and pectin are typically found in abundance, but cellulose is
the predominant polysaccharide and the most abundant source of carbohydrates. However,
25 production of fuel from cellulose poses a difficult technical problem. Some of the factors
for this difficulty are the physical density of lignocelluloses (like wood) that can make
penetration of the biomass structure of lignocelluloses with chemicals difficult and the
chemical complexity of lignocelluloses that lead to difficulty in breaking down the long
chain polymeric structure of cellulose into carbohydrates that can be used to produce fuel.
30 Another factor for this difficulty is the nitrogen compounds and sulfur compounds
contained in the biomass. The nitrogen and sulfur compounds contained in the biomass
can poison catalysts used in subsequent processing.

Most transportation vehicles require high power density provided by internal
combustion and/or propulsion engines. These engines require clean burning fuels which

are generally in liquid form or, to a lesser extent, compressed gases. Liquid fuels are more portable due to their high energy density and their ability to be pumped, which makes handling easier.

Currently, bio-based feedstocks such as biomass provide the only renewable alternative for liquid transportation fuel. Unfortunately, the progress in developing new technologies for producing liquid biofuels has been slow in developing, especially for liquid fuel products that fit within the current infrastructure. Although a variety of fuels can be produced from biomass resources, such as ethanol, methanol, and vegetable oil, and gaseous fuels, such as hydrogen and methane, these fuels require either new distribution technologies and/or combustion technologies appropriate for their characteristics. The production of some of these fuels also tends to be expensive and raise questions with respect to their net carbon savings. There is a need to directly process biomass into liquid fuels.

Processing of biomass as feeds is challenged by the need to directly couple biomass hydrolysis to release sugars, and catalytic hydrogenation/hydrogenolysis/hydrodeoxygenation of the sugar, to prevent decomposition to heavy ends (caramel, or tars). Further, nitrogen and sulfur compounds from the biomass feed can poison the hydrogenation/hydrogenolysis/hydrodeoxygenation catalysts, such as Pt/Re catalysts, and reduce the activity of the catalysts.

Summary of the Invention

It was found desirable to carry out catalytic hydrogenation/hydrogenolysis/hydrodeoxygenation of the biomass with a catalysis system that is tolerant to nitrogen and sulfur and further maintain activity with minimal loss of active metal during the reaction.

In one embodiment, a method comprises: providing lignocellulosic biomass solids in a hydrothermal digestion unit in the presence of a digestive solvent, at least one of ammonia or a source of ammonia, and a supported hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support; heating the lignocellulosic biomass solids and digestive solvent in the presence of hydrogen, supported hydrogenolysis catalyst and the at least one of ammonia or a source of ammonia thereby forming a product solution containing plurality of oxygenated hydrocarbons and ammonia; and recycling at least a portion of the ammonia to the hydrothermal digestion unit.

In an embodiment, a method comprises: (i) providing a lignocellulosic biomass; (ii) contacting the biomass with a digestive solvent to form a pretreated biomass containing soluble carbohydrates; (iii) contacting, in a reaction mixture, the pretreated biomass with hydrogen at a temperature in the range of 150°C to less than 300°C in the presence of at least one of ammonia or a source of ammonia and a supported hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support, to form a product solution containing plurality of oxygenated hydrocarbons and ammonia; and (iv) recycling at least a portion of the ammonia to the reaction mixture or pretreated biomass.

In another embodiment, a composition comprises:

(i) lignocellulosic biomass;

(ii) a hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support;

(iii) water; and

(iv) at least one of ammonia or an ammonia source.

The features and advantages of the invention will be apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the spirit of the invention.

Brief Description of the Drawing

This drawing illustrates certain aspects of some of the embodiments of the invention, and should not be used to limit or define the invention.

Fig. 1 is a schematically illustrated block flow diagram of an embodiment of a process 100 of this invention.

Fig. 2 is a schematically illustrate block flow diagram of another embodiment of a process 200 of this invention.

Detailed Description of the Invention

The invention relates to the hydrothermal hydrocatalytic treatment of the biomass with a catalysis system that is tolerant to nitrogen and sulfur and further maintain activity for a prolonged period with minimal loss of active metal in the catalyst such as cobalt or other non-noble metals, during the reaction with the presence of ammonia or a source of ammonia as a pH buffering agent. Ammonia or a source of ammonia can be recycled as ammonia to form ammonium salt buffer in the hydrothermal hydrocatalytic treatment reaction mixture. It has been found that ammonia or a source of ammonia can be an

effective buffering agent for the hydrothermal hydrocatalytic treatment of biomass that can be recycled as ammonia.

The oxygenated hydrocarbons produced from the process are useful in the production of higher hydrocarbons suitable for use in transportation fuels and industrial chemicals from biomass. The higher hydrocarbons produced are useful in forming transportation fuels, such as synthetic gasoline, diesel fuel, and jet fuel, as well as industrial chemicals. As used herein, the term "higher hydrocarbons" refers to hydrocarbons having an oxygen to carbon ratio less than the oxygen to carbon ratio of at least one component of the biomass feedstock. As used herein the term "hydrocarbon" refers to an organic compound comprising primarily hydrogen and carbon atoms, which is also an unsubstituted hydrocarbon. In certain embodiments, the hydrocarbons of the invention also comprise heteroatoms (i.e., oxygen sulfur, phosphorus, or nitrogen) and thus the term "hydrocarbon" may also include substituted hydrocarbons. The term "soluble carbohydrates" refers to oligosaccharides and monosaccharides that are soluble in the digestive solvent and that can be used as feedstock to the hydrogenolysis reaction (e.g., pentoses and hexoses).

Processing of biomass as feeds is challenged by the need to directly couple biomass hydrolysis to release sugars, and catalytic hydrogenation/hydrogenolysis/hydrodeoxygenation of the sugar, to prevent decomposition to heavy ends (caramel, or tars). Nitrogen and sulfur compounds from the biomass feed can poison the hydrogenation/hydrogenolysis/ hydrodeoxygenation catalysts, such as Pt/Re catalysts, and reduce the activity of the catalysts. Reduced or partially reduced nitrogen or sulfur compounds such as those found in proteins and amino acids present in the biomass feed, are potential poisons for transition metal catalysts used to activate molecular hydrogen for reduction reactions. Oxidized forms of nitrogen or sulfur, in the form of nitrates or sulfates may not poison many catalysts used for hydrogen activation and reduction reactions. Biomass hydrolysis starts above 120 °C and continues through 200 °C. Sulfur and nitrogen compounds can be removed by ion exchange resins (acidic) such as discussed in US publication no. US2012/0152836, that are stable to 120 °C, but the base resins required for complete N,S removal cannot be used above 100 °C (weak base), or 60°C for the strong base resins. Cycling of temperature from 60° C ion exchange to reaction temperatures between 120 – 275 °C represents a substantial energy yield loss. Use of a poison tolerant catalyst in the process to enable direct coupling of biomass hydrolysis and catalytic

hydrogenation / hydrogenolysis/ hydrodeoxygenation of the resulting sugar is an advantage, for a biomass feed process. The methods and systems of the invention have an advantage of using a poison tolerant catalyst for the direct coupling of biomass hydrolysis and catalytic hydrogenation / hydrogenolysis / hydrodeoxygenation of the resulting sugar and other derived intermediates, with minimal loss of active metal over time.

In some embodiments, at least a portion of oxygenated hydrocarbons produced in the hydrogenolysis reaction are recycled within the process and system to at least in part from the *in situ* generated solvent, which is used in the biomass digestion process. This recycle saves costs in provision of a solvent that can be used to extract nitrogen, sulfur, and optionally phosphorus compounds from the biomass feedstock. Further, by controlling the degradation of carbohydrate in the hydrogenolysis process, hydrogenation reactions can be conducted along with the hydrogenolysis reaction at temperatures ranging from 150 °C to 300 °C. As a result, a separate hydrogenation reaction section can optionally be avoided, and the fuel forming potential of the biomass feedstock fed to the process can be increased. This process and reaction scheme described herein also results in a capital cost savings and process operational cost savings. Advantages of specific embodiments will be described in more detail below.

In one embodiment, a method comprises: providing lignocellulosic biomass solids in a hydrothermal digestion unit in the presence of a digestive solvent, at least one of ammonia or a source of ammonia, and a supported hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support; heating the lignocellulosic biomass solids and digestive solvent in the presence of hydrogen, supported hydrogenolysis catalyst and the at least one of ammonia or a source of ammonia thereby forming a product solution containing plurality of oxygenated hydrocarbons and ammonia; and separating and recycling at least a portion of the ammonia to the hydrothermal digestion unit.

In some embodiments, the invention provides methods comprising: providing a biomass feedstock, contacting the biomass feedstock with a digestive solvent in a digestion system to form an intermediate stream comprising soluble carbohydrates, contacting the intermediate stream with hydrogen in the presence of a supported hydrogenolysis catalyst containing (a) sulfur and (b) Mo or W and (c) Co and/or Ni and at least one of ammonia or a source of ammonia to form a plurality of oxygenated hydrocarbons (or oxygenated intermediates) and ammonia, wherein a first portion of the oxygenated hydrocarbons are

recycled to form the solvent and ammonia is recycled to the reaction mixture or digestion system; and contacting a second portion of the oxygenated hydrocarbons with a catalyst to form a liquid fuel.

In another embodiment, a method comprises: (i) providing a biomass containing
5 celluloses, hemicelluloses, lignin, nitrogen compounds and sulfur compounds; (ii) contacting the biomass with a digestive solvent to form a pretreated biomass containing carbohydrates; (iii) contacting, in a reaction mixture, the pretreated biomass directly with hydrogen in the presence of at least one of ammonia or a source of ammonia and a supported hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co and/or Ni
10 incorporated into a suitable support to form a plurality of oxygenated hydrocarbons.

Ammonia or a source of ammonia may be continuously or semi-continuously or periodically or initially added to the reaction system (or reaction mixture) or generated in the reaction mixture to minimize active metal leaching and maintain catalyst activity. Suitable sources of ammonia may be, for example, ammonium carbonate, ammonium
15 propionate, ammonium glycolate, ammonium levulinate, ammonium acetate, ammonium formate, ammonium butyrate, ammonium chloride, and ammonium sulfate. It is desirable to introduce ammonia or a source of ammonia to the reaction mixture (or via pretreated biomass) in an amount sufficient to maintain the pH of the reaction mixture to a desirable pH. In some reaction conditions, the desirable pH may be in the range of 3 to 10,
20 preferably to 4 to 8, more preferably to 5 to 7. In other embodiments, it may be desirable to run the reaction system under more basic conditions. The amount of ammonia or source of ammonia can be adjusted accordingly.

The source of ammonia can be an ammonia salt of a weak acid such as, for example, ammonium acetate or an ammonium salt of a strong acid such as, for example,
25 ammonium sulfate. Ammonia may be generated by adding a strong base such as, for example, KOH or NaOH to the ammonium salt of a strong acid. Such ammonia derivative (source of ammonia) is a base derivable from ammonia.

The ammonia (or source of ammonia) in water as solvent neutralizes acetic acid under pressure.



When heated or when pressure is lowered, the reaction is reversed. The NH_3 gas is the most volatile component, so it drives the equilibrium back to the left, providing NH_3

gas as recycled base.

In some embodiments, lignocellulosic biomass (solids) being continuously or semi-continuously added to the hydrothermal digestion unit may be pressurized before being added to the hydrothermal digestion unit, particularly when the hydrothermal digestion unit is in a pressurized state. Pressurization of the cellulosic biomass solids from atmospheric pressure to a pressurized state may take place in one or more pressurization zones before addition of the cellulosic biomass solids to the hydrothermal digestion unit. Suitable pressurization zones that may be used for pressurizing and introducing lignocellulosic biomass to a pressurized hydrothermal digestion unit are described in more detail in commonly owned United States Patent Application Publications 20130152457 and 20130152458. Suitable pressurization zones described therein may include, for example, pressure vessels, pressurized screw feeders, and the like. In some embodiments, multiple pressurization zones may be connected in series to increase the pressure of the cellulosic biomass solids in a stepwise manner.

In reference to Figure 1, in one embodiment of the invention process 100, biomass **2** is provided to digestion unit **6**, that may have one or more units, containing a supported hydrogenolysis catalyst containing (a) sulfur and (b) Mo or W and (c) Co and/or Ni or mixtures thereof, and a digestive solvent **10** (that may be recycled from the process), and at least one of ammonia or ammonia precursor, whereby when heated with molecular hydrogen **21** produces oxygenated hydrocarbons. The effluent product stream from the digestion unit **28** contains oxygenated hydrocarbons and at least one of ammonia or ammonia precursor. Ammonia may be separated from the product stream **30** by separation, that can be facilitated by heating or reducing pressure in a separation unit **36** (as an example as an overhead stream **25**) that is recycled to the digestion unit **6**. In one embodiment the digester-reactor may be configured as disclosed in a co-pending US application no. 61/720757 filed October 31, 2012 which disclosure is hereby incorporated by reference.

In reference to Figure 2, in one embodiment of the invention process **200**, biomass **102** is provided to digestion zone **106** that may have one or more digester(s), whereby the biomass is contacted with a digestive solvent **110**. The treated biomass pulp **120** contains soluble carbohydrates and other intermediates containing sulfur compounds and nitrogen compounds from the biomass. The sulfur and nitrogen content may vary depending on the biomass source **102**. At least a portion of the treated biomass **120** is catalytically reacted

with hydrogen **121**, in the hydrothermal hydrocatalytic treatment zone **126**, in the presence of a supported hydrogenolysis catalyst containing (a) sulfur and (b) Mo or W and (c) Co and/or Ni and at least one of ammonia or a source of ammonia supplied through a stream containing ammonium hydroxide precursor to produce a product stream **128** containing plurality of oxygenated hydrocarbons and ammonia and/or a source of ammonia; separating ammonia from the product stream (that may be an overhead distillate containing ammonia **125**) and a product stream **130**. At least a portion of the ammonia containing stream is recycled to the reaction mixture in **126** (as in figure 2) or to pretreated biomass via stream **120** (not shown). At least a portion of the oxygenated intermediates may be processed further to produce higher hydrocarbons to form a liquid fuel. The digestion zone **106** and the hydrothermal hydrocatalytic treatment zone **126** may be conducted in the same reactor or in a separate reactor. The treated biomass **120** may be optionally washed prior to contacting in the hydrogenolysis zone (or hydrothermal hydrocatalytic treatment zone) **126**. If washed, water is most typically used as wash solvent.

In another embodiments (not shown), the ammonium hydroxide or an ammonium hydroxide precursor may be introduced with the digestive solvent, with the biomass, with the catalyst, or separately, so long as the ammonium hydroxide or an ammonium hydroxide precursor is present with the supported hydrogenolysis catalyst in the hydrogenolysis zone.

Any suitable (e.g., inexpensive and/or readily available) type of lignocellulosic biomass can be used. Suitable lignocellulosic biomass can be, for example, selected from, but not limited to, forestry residues, agricultural residues, herbaceous material, municipal solid wastes, waste and recycled paper, pulp and paper mill residues, and combinations thereof. Thus, in some embodiments, the biomass can comprise, for example, corn stover, straw, bagasse, miscanthus, sorghum residue, switch grass, bamboo, water hyacinth, hardwood, hardwood chips, hardwood pulp, softwood, softwood chips, softwood pulp, and/or combination of these feedstocks. The biomass can be chosen based upon a consideration such as, but not limited to, cellulose and/or hemicelluloses content, lignin content, growing time/season, growing location/transportation cost, growing costs, harvesting costs and the like.

Prior to treatment with the digestive solvent, the untreated biomass can be washed and/or reduced in size (e.g., chopping, crushing or debarking) to a convenient size and certain quality that aids in moving the biomass or mixing and impregnating the chemicals from digestive solvent. Thus, in some embodiments, providing biomass can comprise

harvesting a lignocelluloses-containing plant such as, for example, a hardwood or softwood tree. The tree can be subjected to debarking, chopping to wood chips of desirable thickness, and washing to remove any residual soil, dirt and the like.

It is recognized that washing with water prior to treatment with digestive solvent is desired, to rinse and remove simple salts such as nitrate, sulfate, and phosphate salts which otherwise may be present, and contribute to measured concentrations of nitrogen, sulfur, and phosphorus compounds present. This wash is accomplished at a temperature of less than 60 degrees Celsius, and where hydrolysis reactions comprising digestion do not occur to a significant extent. Other nitrogen, sulfur, and phosphorus compounds are bound to the biomass and are more difficult to remove, and requiring digestion and reaction of the biomass, to effect removal. These compounds may be derived from proteins, amino acids, phospholipids, and other structures within the biomass, and may be potent catalyst poisons. The poison tolerant catalyst described herein, allows some of these more difficult to remove nitrogen and sulfur compounds to be present in subsequent processing.

In the digestion zone, the size-reduced biomass is contacted with the digestive solvent where the digestion reaction takes place. The digestive solvent must be effective to digest lignins.

In one aspect of the embodiment, the digestive solvent maybe a Kraft-like digestive solvent that contains (i) at least 0.5 wt%, preferably at least 4 wt%, to at most 20 wt%, more preferably to 10 wt%, based on the digestive solvent, of at least one alkali selected from the group consisting of sodium hydroxide, sodium carbonate, sodium sulfide, potassium hydroxide, potassium carbonate, ammonium hydroxide, and mixtures thereof, (ii) optionally, 0 to 3%, based on the digestive solvent, of anthraquinone, sodium borate and/or polysulfides; and (iii) water (as remainder of the digestive solvent). In some embodiments, the digestive solvent may have an active alkali of between 0.5% to 25%, more preferably between 10 to 20%. The term "active alkali"(AA), as used herein, is a percentage of alkali compounds combined, expressed as sodium oxide based on weight of the biomass less water content (dry solid biomass). The digestion is carried out typically at a cooking-liquor to biomass ratio in the range of 2 to 6, preferably 3 to 5. The digestion reaction is carried out at a temperature within the range of from 60 °C, preferably 100 °C, to 270 °C, and a residence time within 0.25 h to 24h. The reaction is carried out under conditions effective to provide a pretreated biomass stream containing pretreated biomass having a lignin content that is less than 20% of the amount in the untreated biomass feed,

and a chemical liquor stream containing alkali compounds and dissolved lignin and hemicellulose material.

The digestion can be carried out in a suitable vessel, for example, a pressure vessel of carbon steel or stainless steel or similar alloy. The digestion zone can be carried out in the same vessel or in a separate vessel. The cooking can be done in continuous or batch mode. Suitable pressure vessels include, but are not limited to the “PANDIATM Digester” (Voest-Alpine Industrienlagenbau GmbH, Linz, Austria), the “DEFIBRATOR Digester” (Sunds Defibrator AB Corporation, Stockholm, Sweden), M&D (Messing & Durkee) digester (Bauer Brothers Company, Springfield, Ohio, USA) and the KAMYR Digester (Andritz Inc., Glens Falls, New York, USA). The digestive solvent has a pH from 10 to 14, preferably around 12 to 13 depending on the concentration of active alkali AA. The contents can be kept at a temperature within the range of from 100 °C to 230 °C for a period of time, more preferably within the range from 130 °C to 180 °C. The period of time can be from 0.25 to 24.0 hours, preferably from 0.5 to 2 hours, after which the pretreated contents of the digester are discharged. For adequate penetration, a sufficient volume of liquor is required to ensure that all the biomass surfaces are wetted. Sufficient liquor is supplied to provide the specified digestive solvent to biomass ratio. The effect of greater dilution is to decrease the concentration of active chemical and thereby reduce the reaction rate.

In a system using the digestive solvent such as a Kraft- like digestive solvent similar to those used in a Kraft pulp and paper process, the chemical liquor may be regenerated in a similar manner to a Kraft pulp and paper chemical regeneration process.

In another embodiment, an at least partially water miscible organic solvent that has partial solubility in water, preferably greater than 2 weight percent in water, may be used as digestive solvent to aid in digestion of lignin, and the nitrogen, and sulfur compounds. In one such embodiment, the digestive solvent is a water- organic solvent mixture with optional inorganic acid promoters such as HCl or sulfuric acid. Oxygenated solvents exhibiting full or partial water solubility are preferred digestive solvents. In such a process, the organic digestive solvent mixture can be, for example, methanol, ethanol, acetone, ethylene glycol, propylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol. Organic acids such as acetic, oxalic, acetylsalicylic and salicylic acids can also be used as catalysts (as acid promoter) in the at least partially miscible organic solvent process. Temperatures for the digestion may range from 130 to 270 °C, preferably from 140 to 220

°C , and contact times from 0.25 to 24 hours, preferably from one to 4 hours. Preferably, a pressure from 2 to 100 bar, and most typically from 5 to 50 bar, is maintained on the system to avoid boiling or flashing away of the solvent.

Optionally the pretreated biomass stream can be washed prior to hydrogenolysis zone depending on the embodiment. In the wash system, the pretreated biomass stream can be washed to remove one or more of non-cellulosic material, and non-fibrous cellulosic material prior to hydrogenolysis. The pretreated biomass stream is optionally washed with a water stream under conditions to remove at least a portion of lignin, hemicellulosic material, and salts in the pretreated biomass stream. For example, the pretreated biomass stream can be washed with water to remove dissolved substances, including degraded, but non-processable cellulose compounds, solubilized lignin, and/or any remaining alkaline chemicals such as sodium compounds that were used for cooking or produced during the cooking (or pretreatment). The washed pretreated biomass stream may contain higher solids content by further processing such as mechanical dewatering as described below.

In a preferred embodiment, the pretreated biomass stream is washed counter-currently. The wash can be at least partially carried out within the digester and/or externally with separate washers. In one embodiment of the invention process, the wash system contains more than one wash steps, for example, first washing, second washing, third washing, etc. that produces washed pretreated biomass stream from first washing, washed pretreated biomass stream from second washing, etc. operated in a counter current flow with the water, that is then sent to subsequent processes as washed pretreated biomass stream. The water is recycled through first recycled wash stream and second recycled wash stream and then to third recycled wash stream. Water recovered from the chemical liquor stream by the concentration system can be recycled as wash water to wash system. It can be appreciated that the washed steps can be conducted with any number of steps to obtain the desired washed pretreated biomass stream. Additionally, the washing may adjust the pH for subsequent steps to the desired pH for the hydrothermal hydrocatalytic treatment. The ammonium hydroxide or an ammonium hydroxide precursor may be optionally added at this step to adjust the pH to the desired pH for the hydrothermal hydrocatalytic treatment.

In one embodiment of the invention process, biomass **102** is provided to digestion zone **106** that may have one or more digestion zones and/or digesting vessels, whereby the

biomass is contacted with a digestive solvent. The digestive solvent is optionally at least a portion recycled from the hydrogenolysis reaction as a recycle stream. The hydrogenolysis recycle stream can comprise a number of components including *in situ* generated solvents, which may be useful as digestive solvent at least in part or in entirety. The term “*in situ*” as used herein refers to a component that is produced within the overall process; it is not limited to a particular reactor for production or use and is therefore synonymous with an in-process generated component. The *in situ* generated solvents may comprise oxygenated intermediates. The digestive process to remove nitrogen, and sulfur compounds may vary within the reaction media so that a temperature gradient exists within the reaction media, allowing for nitrogen, and sulfur compounds to be extracted at a lower temperature than cellulose. For example, the reaction sequence may comprise an increasing temperature gradient from the biomass feedstock **102**. The non-extractable solids may be removed from the reaction as an outlet stream. The treated biomass stream **120** is an intermediate stream that may comprise the treated biomass at least in part in the form of carbohydrates. The composition of the treated biomass stream **120** may vary and may comprise a number of different compounds. Preferably, the contained carbohydrates will have 2 to 12 carbon atoms, and even more preferably 2 to 6 carbon atoms. The carbohydrates may also have an oxygen to carbon ratio from 0.5:1 to 1:1.2. Oligomeric carbohydrates containing more than 12 carbon atoms may also be present. In one embodiment, at least a portion of the digested pulp is contacted with hydrogen in the presence of the supported hydrogenolysis catalyst containing (a) sulfur and (b) molybdenum and/or tungsten and (c) cobalt and/or nickel in the presence of at least one of ammonia or a source of ammonia to produce a plurality of oxygenated hydrocarbons. In another embodiment, lignocellulosic biomass is contacted with hydrogen in the presence of digestive solvent and the supported hydrogenolysis catalyst containing (a) sulfur and (b) molybdenum and/or tungsten and (c) cobalt and/or nickel in the presence of at least one of ammonia or a source of ammonia to produce a plurality of oxygenated hydrocarbons. Ammonia or source of ammonia present in the product stream along with the oxygenated hydrocarbons can be separated in a separation zone or unit **136** or **36** to produce an oxygenated hydrocarbon stream and ammonia that can be recycled to **126** or **6** (or oxygenated intermediate stream). A first portion of the oxygenated hydrocarbon (or oxygenated intermediate stream) from product stream **130** or **30** can be recycled to digestion zone **106** or hydrothermal digestion unit **6**, respectively. A

second portion of the oxygenated hydrocarbon (or oxygenated intermediates stream) is processed to produce higher hydrocarbons to form a liquid fuel.

Use of separate processing zones for steps (ii) and (iii) allows conditions to be optimized for digestion and hydrogenation or hydrogenolysis of the digested biomass components, independent from optimization of the conversion of oxygenated intermediates to monooxygenates, before feeding to step (iv) to make higher hydrocarbon fuels. A lower reaction temperature in step (iii) may be advantageous to minimize heavy ends byproduct formation, by conducting the hydrogenation and hydrogenolysis steps initially at a low temperature. This has been observed to result in an intermediates stream which is rich in diols and polyols, but essentially free of non-hydrogenated monosaccharides which otherwise would serve as heavy ends precursors. The subsequent conversion of mostly solubilized intermediates can be done efficiently at a higher temperature, where residence time is minimized to avoid the undesired continued reaction of monooxygenates to form alkane or alkene byproducts. In this manner, overall yields to desired monooxygenates may be improved, via conducting the conversion in two or more stages.

Solubilization and hydrolysis becoming complete at temperatures around 210 °C, aided by organic acids (e.g., carboxylic acids) formed from partial degradation of carbohydrate components. Some lignin can be solubilized before hemicellulose, while other lignin may persist to higher temperatures. Organic *in situ* generated solvents, which may comprise a portion of the oxygenated intermediates, including, but not limited to, light alcohols and polyols, can assist in solubilization and extraction of lignin and other components.

At temperatures above 120 °C, carbohydrates can degrade through a series of complex self-condensation reactions to form caramelans, which are considered degradation products that are difficult to convert to fuel products. In general, some degradation reactions can be expected with aqueous reaction conditions upon application of temperature, given that water will not completely suppress oligomerization and polymerization reactions.

In certain embodiments, the hydrolysis reaction can occur at a temperature between 20 °C and 270 °C and a pressure between 1 atm and 100 atm. An enzyme may be used for hydrolysis at low temperature and pressure. In embodiments including strong acid and enzymatic hydrolysis, the hydrolysis reaction can occur at temperatures as low as ambient temperature and pressure between 1 bar (100 kPa) and 100 bar (10,100 kPa). In some

embodiments, the hydrolysis reaction may comprise a hydrolysis catalyst (e.g., a metal or acid catalyst) to aid in the hydrolysis reaction. The catalyst can be any catalyst capable of effecting a hydrolysis reaction. For example, suitable catalysts can include, but are not limited to, acid catalysts, base catalysts, metal catalysts, and any combination thereof.

5 Acid catalysts can include organic acids such as acetic, formic, levulinic acid, and any combination thereof. In an embodiment the acid catalyst may be generated in the hydrogenolysis reaction and comprise a component of the oxygenated intermediate stream.

In some embodiments, the digestive solvent may contain an *in situ* generated solvent. The *in situ* generated solvent generally comprises at least one alcohol, ketone, or
10 polyol capable of solvating some of the sulfur compounds, and nitrogen compounds of the biomass feedstock. For example, an alcohol may be useful for solvating nitrogen, sulfur, and optionally phosphorus compounds, and in solvating lignin from a biomass feedstock for use within the process. The *in situ* generated solvent may also include one or more organic acids. In some embodiments, the organic acid can act as a catalyst in the removal
15 of nitrogen and sulfur compounds by some hydrolysis of the biomass feedstock. Each *in situ* generated solvent component may be supplied by an external source, generated within the process, and recycled to the hydrolysis zone, or any combination thereof. For example, a portion of the oxygenated intermediates produced in the hydrogenolysis reaction may be separated in the separator stage for use as the *in situ* generated solvent in the hydrolysis
20 reaction. In an embodiment, the *in situ* generated solvent can be separated, stored, and selectively injected into the recycle stream so as to maintain a desired concentration in the recycle stream.

Each reactor vessel preferably includes an inlet and an outlet adapted to remove the product stream from the vessel or reactor. In some embodiments, the vessel in which at
25 least some digestion occurs may include additional outlets to allow for the removal of portions of the reactant stream. In some embodiments, the vessel in which at least some digestion occurs may include additional inlets to allow for additional solvents or additives.

The digestion may occur in any contactor suitable for solid-liquid contacting. The digestion may for example be conducted in a single or multiple vessels, with biomass
30 solids either fully immersed in liquid digestive solvent, or contacted with solvent in a trickle bed or pile digestion mode. As a further example, the digestion step may occur in a continuous multizone contactor as described in US Patent No. 7285179 (Snekkenes et al., “Continuous Digester for Cellulose Pulp including Method and Recirculation System for

such Digester”). Alternately, the digestion may occur in a fluidized bed or stirred contactor, with suspended solids. The digestion may be conducted batch wise, in the same vessel used for pre-wash, post wash, and/or subsequent reaction steps.

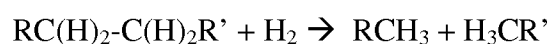
The relative composition of the various carbohydrate components in the treated biomass stream affects the formation of undesirable by-products such as tars or heavy ends in the hydrogenolysis reaction. In particular, a low concentration of carbohydrates present as reducing sugars, or containing free aldehyde groups, in the treated biomass stream can minimize the formation of unwanted by-products. In preferred embodiments, it is desirable to have a concentration of no more than 5 wt%, based upon total liquid, of readily degradable carbohydrates in monomeric form, or heavy end precursors in the treated biomass, while maintaining a total organic intermediates concentration, which can include the oxygenated intermediates (e.g., mono-oxygenates, diols, and/or polyols) derived from the carbohydrates, as high as possible, via use of concerted reaction or rapid recycle of the liquid between the digestion zone, and a catalytic reaction zone converting the solubilized carbohydrates to oxygenated intermediates.

For any of the configurations, a substantial portion of lignin is removed with solvent from digesting step. In one configuration, the remaining lignin, if present, can be removed upon cooling or partial separation of oxygenates from hydrogenolysis product stream, to comprise a precipitated solids stream. Optionally, the precipitated solids stream containing lignin may be formed by cooling the digested solids stream prior to hydrogenolysis reaction. In yet another configuration, the lignin which is not removed with digestion solvent is passed into step (iv), where it may be precipitated upon vaporization or separation of hydrogenolysis product stream, during processing to produce a higher hydrocarbon stream.

The treated biomass stream **120** may comprise C5 and C6 carbohydrates that can be reacted in the hydrogenolysis reaction. For embodiments comprising hydrogenolysis, oxygenated intermediates such as sugar alcohols, sugar polyols, carboxylic acids, ketones, and/or furans can be converted to fuels in a further processing reaction. The hydrogenolysis reaction comprises hydrogen and a hydrogenolysis catalyst to aid in the reactions taking place. The various reactions can result in the formation of one or more oxygenated hydrocarbon (or oxygenated intermediate streams) **130**.

One suitable method for performing hydrogenolysis of carbohydrate-containing biomass includes contacting a carbohydrate or stable hydroxyl intermediate with hydrogen

or hydrogen mixed with a suitable gas and a hydrogenolysis catalyst in a hydrogenolysis reaction under conditions effective to form a reaction product comprising smaller molecules or polyols. Most typically, hydrogen is dissolved in the liquid mixture of carbohydrate, which is in contact with the catalyst under conditions to provide catalytic
5 reaction. At least a portion of the carbohydrate feed is contacted directly with hydrogen in the presence of the hydrogenolysis catalyst. By the term “directly”, the reaction is carried out on at least a portion of the carbohydrate without necessary stepwise first converting all of the carbohydrates into a stable hydroxyl intermediate. As used herein, the term “smaller molecules or polyols” includes any molecule that has a lower molecular weight, which can
10 include a smaller number of carbon atoms or oxygen atoms than the starting carbohydrate. In an embodiment, the reaction products include smaller molecules that include polyols and alcohols. This aspect of hydrogenolysis entails breaking of carbon-carbon bonds, where hydrogen is supplied to satisfy bonding requirements for the resulting smaller molecules, as shown for the example:



where R and R' are any organic moieties.

In an embodiment, a carbohydrate (e.g., a 5 and/or 6 carbon carbohydrate molecule) can be converted to stable hydroxyl intermediates comprising propylene glycol, ethylene glycol, and glycerol using a hydrogenolysis reaction in the presence of a hydrogenolysis
20 catalyst.

The hydrogenolysis catalyst may include a support material that has incorporated therein or is loaded with a metal component, which is or can be converted to a metal compound that has activity towards the catalytic hydrogenolysis of soluble carbohydrates. The support material can comprise any suitable inorganic oxide material that is typically
25 used to carry catalytically active metal components. Examples of possible useful inorganic oxide materials include alumina, silica, silica-alumina, magnesia, zirconia, boria, titania and mixtures of any two or more of such inorganic oxides. The preferred inorganic oxides for use in the formation of the support material are alumina, silica, silica-alumina and mixtures thereof. Most preferred, however, is alumina.

In the preparation of the hydrogenolysis catalyst, the metal component of the catalyst composition may be incorporated into the support material by any suitable method or means that provides the support material that is loaded with an active metal precursor, thus, the composition includes the support material and a metal component. One method of

incorporating the metal component into the support material includes, for example, co-mulling the support material with the active metal or metal precursor to yield a co-mulled mixture of the two components. Or, another method includes the co-precipitation of the support material and metal component to form a co-precipitated mixture of the support material and metal component. Or, in a preferred method, the support material is
5 impregnated with the metal component using any of the known impregnation methods such as incipient wetness to incorporate the metal component into the support material.

When using the impregnation method to incorporate the metal component into the support material, it is preferred for the support material to be formed into a shaped particle comprising an inorganic oxide material and thereafter loaded with an active metal precursor, preferably, by the impregnation of the shaped particle with an aqueous solution of a metal salt to give the support material containing a metal of a metal salt solution. To form the shaped particle, the inorganic oxide material, which preferably is in powder form, is mixed with water and, if desired or needed, a peptizing agent and/or a binder to form a
10 mixture that can be shaped into an agglomerate. It is desirable for the mixture to be in the form of an extrudable paste suitable for extrusion into extrudate particles, which may be of various shapes such as cylinders, trilobes, etc. and nominal sizes such as 1/16", 1/8", 3/16", etc. The support material of the inventive composition, thus, preferably, is a shaped particle comprising an inorganic oxide material.

The calcined shaped particle can have a surface area (determined by the BET method employing N₂, ASTM test method D 3037) that is in the range of from 1 m²/g to 500 m²/g.
20

In one embodiment, the calcined shaped particle is impregnated in one or more impregnation steps with a metal component using one or more aqueous solutions containing at least one metal salt wherein the metal compound of the metal salt solution is an active metal or active metal precursor. The metal elements are (a) molybdenum (Mo) and (b) cobalt (Co) and/or nickel (Ni). Phosphorus (P) can also be a desired component. For Co and Ni, the metal salts include metal acetates, formates, citrates, oxides, hydroxides, carbonates, nitrates, sulfates, and two or more thereof. The preferred metal
25 salts are metal nitrates, for example, such as nitrates of nickel or cobalt, or both. For Mo, the metal salts include metal oxides or sulfides. Preferred are salts containing the Mo and ammonium ion, such as ammonium heptamolybdate and ammonium dimolybdate.
30

Phosphorus is an additive that may be incorporated in these catalysts. Phosphorus may be added to increase the solubility of the molybdenum and to allow stable solutions of cobalt and/or nickel with the molybdenum to be formed for impregnation. Without wishing to be bound by theory, it is thought that phosphorus may also promote hydrogenation and hydrodenitrogenation (HDN). The ability to promote HDN is an important one since nitrogen compounds are known inhibitors of the HDS reaction. The addition of phosphorus to these catalysts may increase the HDN activity and therefore increases the HDS activity as a result of removal of the nitrogen inhibitors from the reaction medium. The ability of phosphorus to also promote hydrogenation is also advantageous for HDS since some of the difficult, sterically hindered sulfur molecules are mainly desulfurized via an indirect mechanistic pathway that goes through an initial hydrogenation of the aromatic rings in these molecules. The promotion of the hydrogenation activity of these catalysts by phosphorus increases the desulfurization of these types of sulfur containing molecules. The phosphorus content of the finished catalyst is typically in a range from 0.1 to 5.0 wt%.

The concentration of the metal compounds in the impregnation solution is selected so as to provide the desired metal content in the final composition of the hydrogenolysis catalyst taking into consideration the pore volume of the support material into which the aqueous solution is to be impregnated. Typically, the concentration of metal compound in the impregnation solution is in the range of from 0.01 to 100 moles per liter.

Cobalt, nickel, or combination thereof can be present in the support material having a metal component incorporated therein in an amount in the range of from 0.5 wt. % to 20 wt. %, preferably from 1 wt. % to 15 wt. %, and, most preferably, from 1 wt. % to 12 wt. %, based on metals components (b) and (c) as metal oxide form; and the molybdenum can be present in the support material having a metal component incorporated therein in an amount in the range of from 1 wt. % to 50 wt. %, preferably from 2 wt. % to 40 wt. %, and, most preferably, from 2 wt. % to 30 wt. %, based on metals components (b) and (c) as metal oxide form. The above-referenced weight percents for the metal components are based on the dry support material and the metal component as the element (change “element” to “metal oxide form”) regardless of the actual form of the metal component.

The metal loaded catalyst may be sulfided prior to its loading into a reactor vessel or system for its use as hydrogenolysis catalyst or may be sulfided, *in situ*, in a gas phase or liquid phase activation procedure. In one embodiment, the liquid soluble carbohydrate

feedstock can be contacted with a sulfur-containing compound, which can be hydrogen sulfide or a compound that is decomposable into hydrogen sulfide, under the contacting conditions of the invention. Examples of such decomposable compounds include mercaptans, CS₂, thiophenes, dimethyl sulfide (DMS), dimethyl sulfoxide (DMSO), sodium hydrogen sulfide, and dimethyl disulfide (DMDS). Also, preferably, the sulfiding is accomplished by contacting the hydrogen treated composition, under suitable sulfurization treatment conditions, with a suitable feed source that contains a concentration of a sulfur compound. The sulfur compound of the hydrocarbon feedstock can be an organic sulfur compound, particularly, one that is derived from the biomass feedstock or other sulfur containing amino-acids such as cysteine.

Suitable sulfurization treatment conditions are those which provide for the conversion of the active metal components of the precursor hydrogenolysis catalyst to their sulfided form. Typically, the sulfiding temperature at which the precursor hydrogenolysis catalyst is contacted with the sulfur compound is in the range of from 150 °C to 450 °C, preferably, from 175 °C to 425 °C, and, most preferably, from 200 °C to 400 °C.

When using a soluble carbohydrate feedstock that is to be treated using the catalyst to sulfide, the sulfurization conditions can be the same as the process conditions under which the hydrogenolysis is performed. The sulfiding pressure generally can be in the range of from 1 bar to 70 bar, preferably, from 1.5 bar to 55 bar, and, most preferably, from 2 bar to 35 bar. The resulting active catalyst typically has incorporated therein sulfur content in an amount in the range of from 0.1 wt. % to 40 wt. %, preferably from 1 wt. % to 30 wt. %, and, most preferably, from 3 wt. % to 24 wt. %, based on metals components (b) and (c) as metal oxide form.

The conditions for which to carry out the hydrogenolysis reaction will vary based on the type of biomass starting material and the desired products (e.g. gasoline or diesel). One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate conditions to use to carry out the reaction. In general, the hydrogenolysis reaction is conducted at temperatures in the range of 110 °C to 300 °C, and preferably of 170 °C to less than 300 °C, and most preferably of 180 °C to 290 °C.

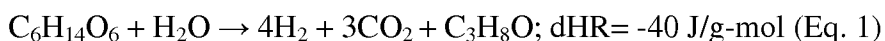
It was found that supplying the buffering agent to the hydrogenolysis reaction mixture during the course of the reaction may prolong catalyst life.

In an embodiment, the hydrogenolysis reaction is conducted at pressures in a range of 0.2 to 200 bar (20 to 20,000 kPa), and preferably in a range of 20 to 140 bar (2000 kPa

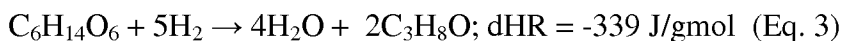
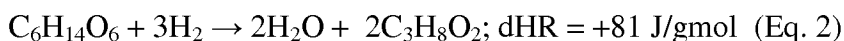
to 14000 kPa), and even more preferably in the range of 50 and 110 bar (5000 to 11000 kPa).

The hydrogen used in the hydrogenolysis reaction of the current invention can include external hydrogen, recycled hydrogen, *in situ* generated hydrogen, and any combination thereof.

In an embodiment, the use of a hydrogenolysis reaction may produce less carbon dioxide and a greater amount of polyols than a reaction that results in reforming of the reactants. For example, reforming can be illustrated by formation of isopropanol (i.e., IPA, or 2-propanol) from sorbitol:



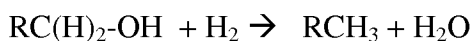
Alternately, in the presence of hydrogen, polyols and mono-oxygenates such as IPA can be formed by hydrogenolysis, where hydrogen is consumed rather than produced:



As a result of the differences in the reaction conditions (e.g., presence of hydrogen), the products of the hydrogenolysis reaction may comprise greater than 25% by mole, or alternatively, greater than 30% by mole of polyols, which may result in a greater conversion in a subsequent processing reaction. In addition, the use of a hydrolysis reaction rather than a reaction running at reforming conditions may result in less than 20% by mole, or alternatively less than 30% by mole carbon dioxide production. As used herein, "oxygenated intermediates" generically refers to hydrocarbon compounds having one or more carbon atoms and between one and three oxygen atoms (referred to herein as C1+O1-3 hydrocarbons), such as polyols and smaller molecules (e.g., one or more polyols, alcohols, ketones, or any other hydrocarbon having at least one oxygen atom).

In an embodiment, hydrogenolysis is conducted under neutral or acidic conditions, as needed to accelerate hydrolysis reactions in addition to the hydrogenolysis. Hydrolysis of oligomeric carbohydrates may be combined with hydrogenation to produce sugar alcohols, which can undergo hydrogenolysis.

A second aspect of hydrogenolysis entails the breaking of -OH bonds such as:



This reaction is also called "hydrodeoxygenation", and may occur in parallel with C-C bond breaking hydrogenolysis. Diols may be converted to mono-oxygenates via this reaction. As reaction severity is increased by increases in temperature or contact time with

catalyst, the concentration of polyols and diols relative to mono-oxygenates will diminish, as a result of this reaction. Selectivity for C-C vs. C-OH bond hydrogenolysis will vary with catalyst type and formulation. Full de-oxygenation to alkanes can also occur, but is generally undesirable if the intent is to produce monooxygenates or diols and polyols which can be condensed or oligomerized to higher molecular weight fuels, in a subsequent processing step. Typically, it is desirable to send only mono-oxygenates or diols to subsequent processing steps, as higher polyols can lead to excessive coke formation on condensation or oligomerization catalysts, while alkanes are essentially unreactive and cannot be combined to produce higher molecular weight fuels.

Thus, in the reaction zone the reaction mixture may contain:

(i) lignocellulosic biomass;

(ii) a hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support;

(iii) water; and

(iv) at least one of ammonia or an ammonia source.

In some embodiment, the composition may further comprise (v) digestive organic solvent.

In another embodiment, the catalyst may further comprise (d) phosphorus.

In an embodiment of the invention, the pretreated biomass containing carbohydrates may be converted into an stable hydroxyl intermediate comprising the corresponding alcohol derivative through a hydrogenolysis reaction in addition to an optional hydrogenation reaction in a suitable reaction vessel (such as hydrogenation reaction as described in co-pending patent application publication nos. US20110154721 and US20110282115).

The oxygenated intermediate stream **130** may then pass from the hydrogenolysis system to a further processing stage. In some embodiments, optional separation stage includes elements that allow for the separation of the oxygenated hydrocarbons into different components. In some embodiments of the present invention, the separation stage can receive the oxygenated intermediate stream **130** from the hydrogenolysis reaction and separate the various components into two or more streams. For example, a suitable separator may include, but is not limited to, a phase separator, stripping column, extractor, filter, or distillation column. In some embodiments, a separator is installed prior to a processing reaction to favor production of higher hydrocarbons by separating the higher polyols from the oxygenated intermediates. In such an embodiment, the higher polyols can

be recycled back through to the hydrogenolysis reaction, while the other oxygenated intermediates are passed to the processing reaction. In addition, an outlet stream from the separation stage containing a portion of the oxygenated intermediates may act as *in situ* generated digestive solvent when recycled to the digester **106**. In one embodiment, the separation stage can also be used to remove some or all of the lignin from the oxygenated intermediate stream. The lignin may be passed out of the separation stage as a separate stream, for example as output stream.

In an embodiment, the processing reaction may comprise a condensation reaction to produce a fuel blend. In an embodiment, the higher hydrocarbons may be part of a fuel blend for use as a transportation fuel. In such an embodiment, condensation of the oxygenated intermediates occurs in the presence of a catalyst capable of forming higher hydrocarbons. While not intending to be limited by theory, it is believed that the production of higher hydrocarbons proceeds through a stepwise addition reaction including the formation of carbon-carbon bond. The resulting reaction products include any number of compounds, as described in more detail below.

Referring to Figure 1, in some embodiments, an outlet stream **130** containing at least a portion of the oxygenated intermediates can pass to a processing reaction or processing reactions. Suitable processing reactions may comprise a variety of catalysts for condensing one or more oxygenated intermediates to higher hydrocarbons, defined as hydrocarbons containing more carbons than the oxygenated intermediate precursors. The higher hydrocarbons may comprise a fuel product. The fuel products produced by the processing reactions represent the product stream from the overall process at higher hydrocarbon stream. In an embodiment, the oxygen to carbon ratio of the higher hydrocarbons produced through the processing reactions is less than 0.5, alternatively less than 0.4, or preferably less than 0.3.

The oxygenated intermediates can be processed to produce a fuel blend in one or more processing reactions. In an embodiment, a condensation reaction can be used along with other reactions to generate a fuel blend and may be catalyzed by a catalyst comprising acid or basic functional sites, or both. In general, without being limited to any particular theory, it is believed that the basic condensation reactions generally consist of a series of steps involving: (1) an optional dehydrogenation reaction; (2) an optional dehydration reaction that may be acid catalyzed; (3) an aldol condensation reaction; (4) an optional ketonization reaction; (5) an optional furanic ring opening reaction; (6) hydrogenation of

the resulting condensation products to form a C₄+ hydrocarbon; and (7) any combination thereof. Acid catalyzed condensations may similarly entail optional hydrogenation or dehydrogenation reactions, dehydration, and oligomerization reactions. Additional polishing reactions may also be used to conform the product to a specific fuel standard, including reactions conducted in the presence of hydrogen and a hydrogenation catalyst to remove functional groups from final fuel product. A catalyst comprising a basic functional site, both an acid and a basic functional site, and optionally comprising a metal function, may be used to effect the condensation reaction.

In an embodiment, the aldol condensation reaction may be used to produce a fuel blend meeting the requirements for a diesel fuel or jet fuel. In an embodiment of the present invention, the fuel yield of the current process may be greater than other bio-based feedstock conversion processes. Without wishing to be limited by theory, it is believed that the presence of the ammonium hydroxide or an ammonium hydroxide precursor with the nitrogen and sulfur tolerant catalyst used in process prolongs such catalyst life by preventing the leaching of active metal such as cobalt.

To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the invention.

EXAMPLES

Example 1: Ammonia buffer

A 75-milliliter Parr5000 reactor was charged with 30.21 grams of 50 wt% glycerol in deionized water, 0.202 grams of ammonium carbonate buffer, and 0.304 grams of the catalyst (DC-2534, containing 1–10% cobalt oxide and molybdenum trioxide (up to 30 wt%) on alumina, and less than 2% nickel), obtained from Criterion Catalyst & Technologies L.P., and sulfided by the method described in US2010/0236988 Example 5.

The reactor was pressured to 53 bar with hydrogen and heated to 250 °C for 5 hours. A final pH of 5.6 was obtained, indicating effective buffering of acetic and other acids formed as a byproduct of reaction

Reactor product was analyzed by gas chromatography using a 60-m x 0.32 mm ID DB-5 column of 1 µm thickness, with 50:1 split ratio, 2 ml/min helium flow, and column oven at 40 °C for 8 minutes, followed by ramp to 285 °C at 10°C/min, and a hold time of 53.5 minutes. The injector temperature was set at 250 °C, and the detector temperature was set at 300 °C. GC analysis indicated 26% conversion of glycerol, with 1,2-propylene glycol the dominant product formed, along with a few weight percent of ethanol and propanol.

Example 2: Distillation with ammonia buffer

The reactor contents from Example 1 were distilled in a short path still at atmospheric pressure, under a blanket of nitrogen. The distillation was continued at a bottoms temperature from 142.5 to 245 °C, to yield 50.1% of the initial charge as an overhead product. The pH of the distillate averaged to 7.5, while a pH of 8.6 was obtained for the final distillate sample comprising 8% of the initial charge. The pH of the remaining bottoms fraction was 6.6.

This example demonstrates the ability to distill the ammonia buffer overhead as base, which can be recycled to neutralize acidity in a subsequent reaction cycle.

Example 3 and 4: Buffer recycle

Two 75-milliliter Parr5000 reactors were charged with 10 grams of deionized water as solvent, 0.25 grams of the DC-2534 catalyst from example 1, and 2.7 grams of southern pine mini-chips (39% moisture). 10 grams of combined overhead distillate from example 2 (pH 8.6) were added to the reactor in example 3. For example 4, 10-grams of deionized water were added.

Both reactors were pressured to 52 bar with hydrogen and heated to 190 °C for 1 hour, followed by heating to 250 °C for 4 hours, stirred. Following the digestion and reaction, both reactors were cooled and depressured, then opened and reactor contents filtered via Whatman GF/F filter paper to assess the percentage of digested wood solids.

- 5 Digestion was virtually complete for both reactors. However, the pH for example 3 with added overhead distillate was 3.5 at the end of reaction, compare to a pH of 2.8 where deionized water was added in place of the distillate fraction.

GC analysis indicated two fold higher concentrations of targeted monooxygenate and glycol intermediates for example 3 with added distillate, vs. example 4.

- 10 This result demonstrates an ability to buffer the biomass digester reactor to obtain a higher pH, *via* recycle of overheaded distillate from examples 1 and 2 where ammonium carbonate was used as buffer, followed by distillation.

CLAIMS

1. A method comprising: (i) providing lignocellulosic biomass solids in a hydrothermal digestion unit in the presence of a digestive solvent, at least one of ammonia or a source of ammonia, and a supported hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support; (ii) heating the lignocellulosic biomass solids and digestive solvent in the presence of hydrogen, supported hydrogenolysis catalyst and the at least one of ammonia or a source of ammonia thereby forming a product solution containing plurality of oxygenated hydrocarbons and ammonia; and (iii) recycling at least a portion of the ammonia to the hydrothermal digestion unit.

2. A method comprising: (i) providing a lignocellulosic biomass; (ii) contacting the biomass with a digestive solvent to form a pretreated biomass containing soluble carbohydrates; (iii) contacting, in a reaction mixture, the pretreated biomass with hydrogen at a temperature in the range of 150°C to less than 300°C in the presence of at least one of ammonia or a source of ammonia and a supported hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support, to form a product solution containing plurality of oxygenated hydrocarbons and ammonia; and (iv) recycling at least a portion of the ammonia to the reaction mixture or to the pretreated biomass.

3. The method according to claim 1 or claim 2, where the source of ammonia is selected from the group consisting of: ammonium carbonate, ammonium propionate, ammonium glycolate, ammonium levulinate, ammonium acetate, ammonium formate, ammonium butyrate, ammonium chloride, and ammonium sulfate.

4. The method according to claim 3 wherein the source of ammonia is an ammonium salt.

5. The method according to any of claims 1 to 4, wherein ammonia is provided to the reaction mixture.

6. The method according to any of claims 1 to 5 wherein ammonia is generated external to the reaction mixture.

7. The method according to any of claims 1 to 5, wherein the source of ammonia is provided by addition of strong base to an ammonium salt of a strong acid.

8. The method according to claim 7, wherein the strong base is KOH or NaOH

and the ammonium salt is ammonium sulfate.

9. The method according to any of claims 1 to 8, wherein a first portion of the oxygenated hydrocarbons are recycled to form in part the digestive solvent.

10. The method according to claim 2, wherein a first portion of the oxygenated hydrocarbons are recycled to form in part the solvent in step (ii).

11. The method according to claim 2 or claim 10, wherein ammonia is recycled with the first portion of the oxygenated hydrocarbons.

12. The method according to claim 2 or claim 10, wherein the ammonia is recycled separately as an ammonia stream to the reaction mixture or pretreated biomass.

13. The method according to any of claims 1 to 12, wherein sulfur content of the catalyst is in the range of 0.1 wt% to 40wt% based on components (b) and (c) as metal oxide form.

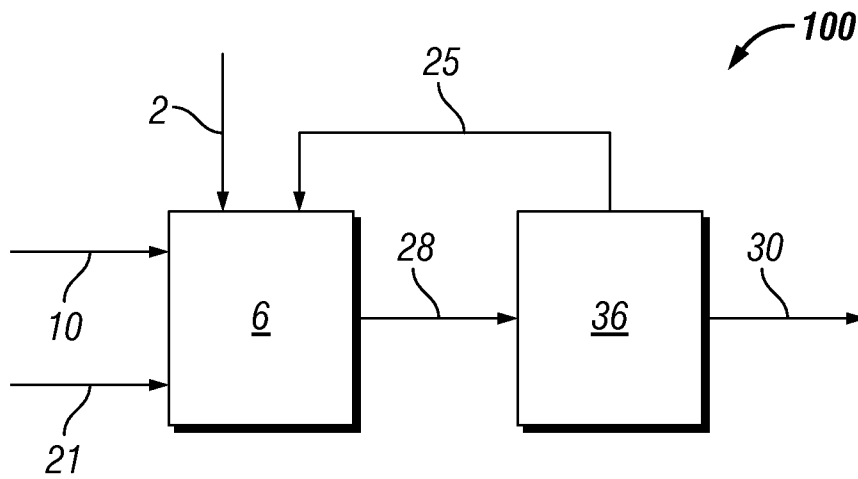
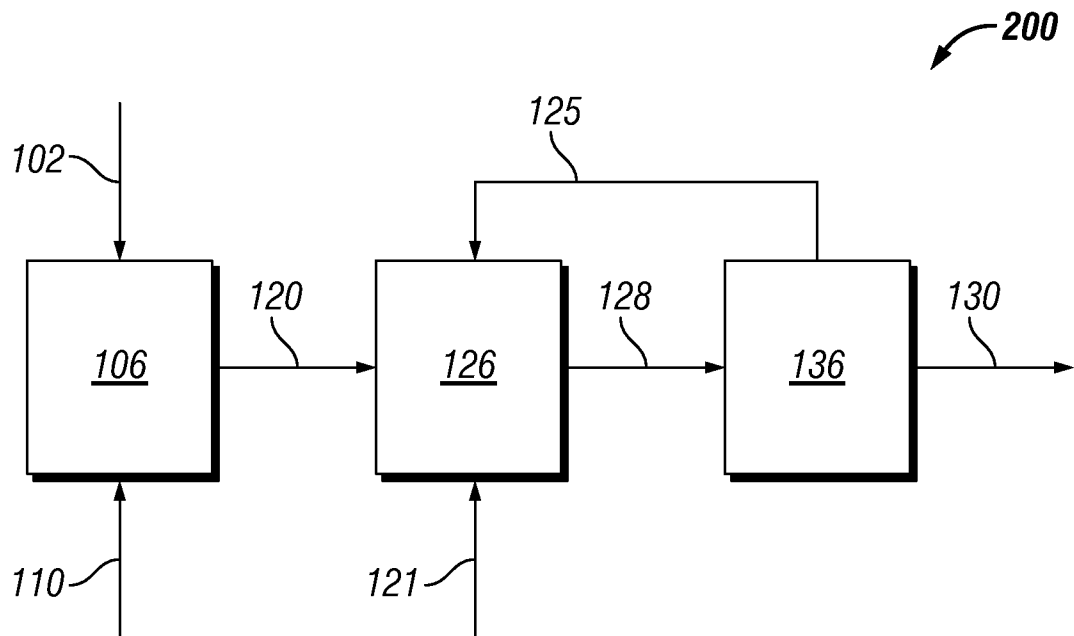
14. The method according to any of claims 1 to 13, wherein the Co and/or Ni content of the catalyst is in the range of 0.5 wt. % to 20 wt. % based on components (b) and (c) as metal oxide form.

15. A composition comprising:
(i) lignocellulosic biomass;
(ii) hydrogenolysis catalyst containing (a) sulfur, (b) Mo or W, and (c) Co, Ni or mixture thereof, incorporated into a suitable support;
(iii) water; and
(iv) at least one of ammonia or a source of ammonia.

16. The composition according to claim 15 wherein the composition further comprises (v) digestive organic solvent.

17. The composition according to claim 15 or claim 16, wherein component (iv) is selected from the group consisting of ammonia, ammonium carbonate, ammonium propionate, ammonium glycolate, ammonium levulinate, ammonium acetate, ammonium formate, ammonium butyrate, ammonium chloride, and ammonium sulfate.

18. The composition according to any of claims 15 to 17, wherein the catalyst further comprises (d) phosphorus.

1/1**FIG. 1****FIG. 2**