

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

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 June 2015 (25.06.2015)

(10) International Publication Number
WO 2015/095457 A1

- (51) **International Patent Classification:**
C10G 1/06 (2006.01) *C07G 1/00* (2011.01)
C10G 3/00 (2006.01) *C08L 1/02* (2006.01)
- (21) **International Application Number:** PCT/US2014/071043
- (22) **International Filing Date:** 18 December 2014 (18.12.2014)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:** 61/917,414 18 December 2013 (18.12.2013) US
- (71) **Applicant (for US only): SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463 (US).
- (71) **Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 The Hague (NL).
- (72) **Inventors: POWELL, Joseph Broun;** 10506 Normont Drive, Houston, Texas 77070 (US). **CHHEDA, Juben Nemchand;** 1255 Eldridge Pkwy, Apt. 504, Houston, Texas 77077 (US).
- (74) **Agent: IWATA, Yukiko;** Shell Oil Company, One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, 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, 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, ST, 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:**
— with international search report (Art. 21(3))



WO 2015/095457 A1

(54) **Title:** BIOMASS TREATMENT FOR HYDROTHERMAL HYDROCATALYTIC CONVERSION

(57) **Abstract:** A selective removal of chlorine and phosphorus that are detrimental to subsequent hydrothermal hydrocatalytic conversion from the biomass feed prior to carrying out catalytic hydrogenation/hydrogenolysis/ hydrodeoxygenation of the biomass in a manner that does not reduce the effectiveness of the hydrothermal hydrocatalytic treatment while minimizing the amount of water used in the process is provided.

BIOMASS TREATMENT FOR HYDROTHERMAL HYDROCATALYTIC CONVERSION

The present application claims the benefit of pending U.S. Provisional Patent
5 Application Serial No. 61/917414, filed December 18, 2013.

Field of the Invention

The invention relates to treatment of biomass for the hydrothermal hydrocatalytic
treatment in the production of higher hydrocarbons suitable for use in transportation fuels
and industrial chemicals from biomass. More specifically, the invention relates to removal
10 of detrimental species from the biomass for an effective biomass hydrothermal
hydrocatalytic conversion.

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
15 shows promise as a fossil fuel alternative. As opposed to fossil fuel, biomass is also
renewable.

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
20 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
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
25 hemicellulose. Hemicellulose and pectin are typically found in abundance, but cellulose is
the predominant polysaccharide and the most abundant source of carbohydrates. However,
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
30 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.
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
5 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
10 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
15 fuels, amenable to existing infrastructure.

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, it is a challenge to minimize generation of waste products that may require
20 treating before disposal and/or catalyst deactivation by poisons.

Summary of the Invention

It was found desirable to remove chlorine and phosphorus from the biomass feed prior to carrying out catalytic hydrogenation/hydrogenolysis/hydrodeoxygenation of the biomass in a manner that does not reduce the effectiveness of the hydrothermal
25 hydrocatalytic treatment while minimizing the amount of water used in the process.

In one embodiment, a method for selective removal of chlorine and phosphorus from a cellulosic biomass solid is provided comprising:

- a. providing a detrimental species-containing cellulosic biomass solids;
- b. introducing said detrimental species-containing cellulosic biomass solids
30 from an inlet into a treatment vessel, said cellulosic biomass solids having a true interstitial volume in said vessel;
- c. introducing a base solution having a pH of greater than 9 from an inlet to said cellulosic biomass solids containing vessel at a temperature in the range of

0°C to 60°C in an amount to fill at least about 5% bed volume to at most about 40% bed volume of said true interstitial volume;

- 5
- d. subsequently to step c, introducing an aqueous solution having a pH of at most 8 from an inlet to said basic cellulosic biomass solids-containing vessel, thereby producing washed cellulosic biomass solids having reduced detrimental species content compared to the detrimental species-containing cellulosic biomass solids and a basic water effluent, wherein said basic water effluent is in the range of about 3 parts to about 0.5 parts relative to about 1 part of detrimental species-containing cellulosic biomass solids (dry basis);
- 10
- e. introducing a removal stream comprising a gas stream or an organic solvent solution from an inlet to the vessel containing the washed cellulosic biomass solids thereby producing a pretreated cellulosic biomass solids with reduced water content compared to the water washed cellulosic biomass solids and an aqueous effluent;
- 15
- f. discharging the pretreated cellulosic biomass solids from an outlet and transferring at least a portion of the discharged pretreated biomass solids to a digestion and/or reaction zone;
- g. recycling at least a first portion of the aqueous effluent to produce base solution; and
- 20
- h. recycling at least a second portion of the aqueous effluent as an aqueous solution.

In yet another embodiment, in the digestion and/or reaction zone of the above methods, the treated cellulosic biomass is contacted with a hydrothermal hydrocatalytic catalyst in the presence of hydrogen and a digestion solvent thereby producing an intermediate oxygenated product stream comprising oxygenated hydrocarbons and water; and at least a portion of the water is separated and recycled to form at least a portion of the aqueous solution.

25

In yet another embodiment, in the digestion and/or reaction zone in the above methods, the treated cellulosic biomass is contacted with a hydrothermal hydrocatalytic catalyst in the presence of hydrogen and a digestion solvent thereby producing an intermediate oxygenated product stream; at least a portion of the oxygenated intermediate product stream is converted to a hydrocarbon product stream comprising hydrocarbons and

30

water; and at least a portion of the water is separated and recycled to form at least a portion of the aqueous solution. The oxygenated intermediate product steam may comprise oxygenated hydrocarbons and water, and at least a portion of the water maybe separated and recycled to form at least a portion of the aqueous solution.

5 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.

Detailed Description of the Invention

10 In one embodiment, the invention relates to selective removal of chlorine and phosphorus, from a cellulosic biomass solids. 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, wood, forestry residues, agricultural residues, herbaceous material, municipal solid wastes, pulp and paper mill residues, and combinations thereof. Thus, in some embodiments, the biomass can
15 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
20 location/transportation cost, growing costs, harvesting costs and the like. These cellulosic biomass solids contain chlorine and phosphorus species that are detrimental to catalysts or equipment used in the hydrothermal hydrocatalytic treatment of the biomass (“detrimental species”). Hence, it is desirable to at least in part remove phosphorus and chlorine species from the cellulosic biomass solids before the hydrothermal hydrocatalytic treatment of
25 biomass.

 The oxygenated hydrocarbons produced from the hydrothermal hydrocatalytic 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,
30 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. As used herein, the term “soluble carbohydrates” refers to monosaccharides or polysaccharides that become solubilized in a digestion process. Although the underlying chemistry is understood behind digesting cellulose and other complex carbohydrates and further transforming simple carbohydrates into organic compounds reminiscent of those present in fossil fuels, high-yield and energy-efficient digestion processes suitable for converting cellulosic biomass into fuel blends have yet to be developed. In this regard, the most basic requirement associated with converting cellulosic biomass into fuel blends using digestion and other processes is that the energy input needed to bring about the conversion should not be greater than the available energy output of the product fuel blends. Further the process should maximize product yield while minimizing waste products. These basic requirements lead to a number of secondary issues that collectively present an immense engineering challenge that has not been solved heretofore.

Further, the removal of these detrimental species is complicated by the sensitivity of the catalysts for the hydrothermal hydrocatalytic treatment to the reaction conditions. 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). For example, too much water from a wash process can dilute the reaction stream and require removal of larger amounts of water from the process and may further lead to stress on the catalyst used in the process. Further, removal of water at a later stage by thermally separating the water will require a large amount of energy. It is also desirable to recycle the wash water to minimize or eliminate the need for other water inputs to the process.

In further embodiment, the invention relates recycling the water used to wash the biomass and to minimizing the amount of waste water generated in the process. The invention balances the competing advantage of selective removal of chlorine and phosphorus, from cellulosic biomass solids while not reducing the effectiveness of the hydrothermal hydrocatalytic treatment while minimizing the amount of water used in the process. Applicants have found that washing the biomass with base solution at low temperature effectively removes at least a portion of the chlorine and phosphorus the biomass without removal of carbohydrates. However a large amount of water required to

remove the chlorine and phosphorus species also hinders and/or creates more process water that requires more water removal and disposals. The process of the invention provides effective solutions to these problems.

It is also important in the wash process to prevent the hydrolysis of wood and loss
5 of carbohydrate to the wash effluent (or aqueous solution effluent). Thus it is preferable to maintain the treatment of the biomass to at most about 60°C. The loss of carbohydrate is preferably less than 10% by weight, more preferably less than 5% by weight, even more preferably less than 2% by weight based on the carbohydrates present in the biomass (dry basis).

10 Prior to treatment, the untreated biomass can be 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
15 debarking, chopping to wood chips of desirable thickness, and washing to remove any residual soil, dirt and the like.

It is preferable to render the biomass feed (wood chips or other) free of entrained air, and densified to insure the feedstock will sink in water or solvent, vs. float (pre-conditioning). Floating can occur if the feed is allowed to dry during storage, upon which
20 air may enter pores and be transported into the process.

Densification via impregnation with water or solvent may be effected by soaking in water or solvent. Pressurization of the water or solvent will force liquid into pores. One of the most effective ways to drive gas (air or non-condensibles) out of the pore of the biomass is to contact the biomass with solvent vapor, most preferable water vapor or
25 steam.

Typically, this is done by supplying low pressure steam (nominal 1 - 2 atmospheres above ambient pressure) to the bottom of a storage bin, and allowing the steam or solvent vapor to travel upwards through the bin of solids, to drive out air or entrained gas. Contacting of water or solvent vapor at a temperature above the biomass temperature
30 results in condensation of liquid water or vapor in the pores of the biomass, driving gas out of the pores. This saturates and densifies the biomass such that it now has a density greater than water or solvent, and therefore sinks when added to liquid water or solvent during the wash process.

The time and duration of the steaming should be controlled such that the temperature of the biomass does not exceed about 60 degrees centigrade for an extended period of time. Specifically, one can supply steam at temperatures above 100 degrees centigrade (the boiling point of water), to biomass initially at ambient temperature (below
5 about 35 degrees centigrade), for a period of time such that the final temperature of the biomass does not exceed about 60 degrees centigrade, or if temperature above 60 degree centigrade, the exposure at this temperature is limited to less than 60 minutes, preferably less than 30 minutes, and most preferably less than about 10 minutes. By minimizing the exposure to temperatures above 60 °C, hydrolysis and degradation of carbohydrate
10 components is minimized, and loss of these components to the water and/or acid and base wash process steps can be minimized to less than 5% of the carbohydrate portion of the biomass, most preferably less than 1%.

The detrimental species-containing cellulosic biomass solids is introduced in to a treatment vessel from an inlet, thus the cellulosic biomass solids have a true interstitial
15 volume in such vessel.

The vessel can be in any shape that include, for example, vertical, horizontal, incline, and may include bends, curves or u shape. The vessel will further have at least one inlet and at least one outlet.

Interstitial volume is the drainable volume of liquid in the bed, not occupied by
20 liquid-saturated biomass. It may be determined by first filling a vessel with biomass that has been pre-densified e.g. by steaming, to insure that it will not float when water, aqueous mixtures, or solvent is introduced to the vessel. Interstitial volume can best be determined by filling upflow with liquid from the bottom of the vessel, after initially filling the vessel with biomass saturated with water or solvent. The interstitial volume is the amount of
25 liquid added to just cover the top of the biomass bed.

In one embodiment, a base solution having a pH of greater than 9, preferably having a pH of at least 10, preferably having a pH of at most 13, more preferably having a pH in the range of 10 to 13, at a temperature in the range of 0°C to 60°C, preferably in the range of 10 to 45°C, is introduced from an inlet to the cellulosic biomass solids containing
30 vessel to obtain an basic cellulosic biomass solids-containing biomass. The inlet may be the same inlet as the biomass solids introduction or a separate, second inlet to the treatment vessel. The base solution is introduced in an amount to fill at least about 5% bed volume to at most about 40% bed volume of such true interstitial volume.

After the base solution introduction, an aqueous solution having a pH of at most 9 is introduced from an inlet to the basic cellulosic biomass solids-containing vessel producing washed cellulosic biomass solids having reduced detrimental species content compared to the detrimental species-containing cellulosic biomass solids and a basic water effluent. The inlet may be the same inlet as the biomass solids introduction, the base solution inlet, or a separate, second or third inlet to the treatment vessel. The basic water effluent and the treated cellulosic biomass solids may be removed from the treatment vessel from the same outlet or a separate, second, outlet.

The base wash is carried out so that the amount of the basic water effluent from the treatment vessel is in the range of about 3 parts to about 0.5 parts, preferably in the range of about 2 parts to about 1 part relative to the cellulosic biomass solids (dry basis) charged to the treatment step, based on weight.

After introduction of aqueous solution, a gas stream or an organic solvent solution is introduced to the vessel containing the washed cellulosic biomass solids, producing a pretreated cellulosic biomass solids with reduced water content compared to the water washed cellulosic biomass solids and an aqueous effluent. The inlet may be the same inlet as the biomass solids introduction, the aqueous solution inlet or a separate, second, or third inlet to the treatment vessel. The aqueous effluent and the pretreated cellulosic biomass solids may be removed from the treatment vessel from the same outlet or a separate, second or third, outlet. In this water displacement step, the water content is reduced by at least by 5% by volume, preferably at least by 25% by volume, more preferably at least by 50% by volume, based on the liquid constituent of the water washed cellulosic biomass solids. The gas may be air, hydrogen, nitrogen, steam, organic vapors, and mixtures thereof. The organic solvent is preferably in situ generated. Preferably, the organic solvent is a solvent (digestive solvent) used in the digestion and/or reaction zone.

The pretreated cellulosic biomass solids is discharged from an outlet of the treatment vessel, and then transferred to a digestion and/or reaction zone.

At least a portion of the aqueous effluent is recycled to produce base solution and/or aqueous solution.

The base solution may contain an inorganic base such as, for example, KOH, NaOH and ammonia. The base content of the base solution is preferably less than 5 Normal and at least 0.01 Normal. The base concentration is preferably from about 0.1 to about 5 Normal.

The maximum density of cellulosic biomass when loaded into a vessel or container to conduct the treatments steps with a free (non-absorbed) liquid phase will be such that the amount of water used for these treatments is less than the total amount of liquid required to fill the vessel or container. Use of recycle treatment water and limited amount of water, as
5 described in the present invention, is therefore required in order to produce an effluent separated from the biomass which contains a maximum concentrations of the detrimental removed components, in the restricted amounts of water treatment allowed. The amounts of water prescribed will typically correspond to the natural water content of the biomass feedstock, augmented by any water which can be made in process conversion steps such as
10 reaction of biomass with hydrogen, with zero or minimal use of additional water from another source. The amount of additional water required is thus restricted to less than 50% of the biomass feed (dry basis), and hence would represent less than a third of the typical amount of additional water employed for similar processing in the manufacture of, for example, pulp used to make paper. Preferably, the amount of additional makeup water
15 above the water naturally present in the biomass feed, and made in the process, is negligible or zero.

At least a portion of the treated cellulosic biomass solids is provided to a digestion and/or reaction zone (collectively referred to as “hydrothermal hydrocatalytic reaction zone”) for further processing. This zone may be conducted in a single step or in multiple
20 steps or vessels as described below.

Preferably, chlorine is reduced by at least 50%, at least 55%, at least 60%, at least 75%, and at least 95 %. Preferably phosphorus is reduced by at least 75st%, at least 80%, at least 85%, at least 90 %, at least 95%, even at least 98 % or essentially completely. The term “essentially completely” means the specie is completely removed within the detection
25 limit or within statistical significance or within measurement errors.

For the instant biofuels process, the minimization of fresh water usage is a key issue. However, due to biomass packing density being poor, at best 3 parts or more of bed volume of water are required to typically fill a bed for washing one part of biomass. In the invention process, the detrimental species is removed with less than 5 parts, preferably at
30 most 2.5 parts, more preferably at most 2 parts, even at most 1.5 parts of water for washing one part of biomass. It is preferred that for the removal process, only the water from the water in the biomass and water generated in the process.

For the hydrothermal catalytic reaction zone, the zone may have one or more vessels. In one embodiment in the digestion/reaction zone hydrolysis and hydrothermal hydrocatalytic reaction of the treated biomass is carried out in one or more vessels. These vessels may be digesters or reactors or combination thereof including a combination
5 hydrothermal hydrocatalytic digestion unit.

In some embodiments, lignocellulosic biomass (solids) being continuously or semi-continuously added to the hydrothermal digestion unit or hydrothermal hydrocatalytic digestion unit may be pressurized before being added to the unit, particularly when the hydrothermal (hydrocatalytic) digestion unit is in a pressurized state. Pressurization of the
10 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 (hydrocatalytic) digestion unit. Suitable pressurization zones that may be used for pressurizing and introducing lignocellulosic biomass to a pressurized hydrothermal digestion unit or hydrothermal hydrocatalytic digestion unit are described in
15 more detail in commonly owned United States Patent Application Publications US20130152457 and US20130152458. 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. The digestion and the
20 hydrothermal hydrocatalytic reaction in the hydrothermal catalytic reaction zone (or digestion reaction zone) may be conducted separately, partially combined, or *in situ*.

In some embodiments, the digestion rate of cellulosic biomass solids may be accelerated in the presence of a liquid phase containing a digestion solvent. In some instances, the liquid phase may be maintained at elevated pressures that keep the digestion
25 solvent in a liquid state when raised above its normal boiling point. Although the more rapid digestion rate of cellulosic biomass solids under elevated temperature and pressure conditions may be desirable from a throughput standpoint, soluble carbohydrates may be susceptible to degradation at elevated temperatures. One approach for addressing the degradation of soluble carbohydrates during hydrothermal digestion is to conduct an *in situ*
30 catalytic reduction reaction process so as to convert the soluble carbohydrates into more stable compounds as soon as possible after their formation.

In certain embodiments, a slurry catalyst may be effectively distributed from the bottom of a charge of cellulosic biomass solids to the top using upwardly directed fluid

flow to fluidize and upwardly convey slurry catalyst particulates into the interstitial spaces within the charge for adequate catalyst distribution within the digesting cellulosic biomass solids. Suitable techniques for using fluid flow to distribute a slurry catalyst within cellulosic biomass solids in such a manner are described in commonly owned United States
5 Published Patent Applications US20140005445 and US20140005444. In addition to affecting distribution of the slurry catalyst, upwardly directed fluid flow may promote expansion of the cellulosic biomass solids and disfavor gravity-induced compaction that occurs during their addition and digestion, particularly as the digestion process proceeds and their structural integrity decreases. Methods of effectively distributing molecular
10 hydrogen within cellulosic biomass solids during hydrothermal digestion is further described in commonly owned United States Published Patent Applications US20140174433 and US20140174432.

In another embodiment the hydrothermal hydrocatalytic digestion unit may be configured as disclosed in a co-pending United States Published Patent Application No.
15 US20140117276. 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 some embodiments, at least a portion of oxygenated hydrocarbons produced in the hydrothermal hydrocatalytic reaction zone are recycled within the process and system
20 to at least in part from the *in situ* generated solvent, which is used in the biomass digestion process. Further, by controlling the degradation of carbohydrate in the hydrothermal hydrocatalytic reaction (e.g., hydrogenolysis process), hydrogenation reactions can be conducted along with the hydrogenolysis reaction at temperatures ranging from about 150 °C to 300 °C. As a result, a separate hydrogenation reaction section can optionally be
25 avoided, and the fuel forming potential of the biomass feedstock fed to the process can be increased. Further, it may be advantageous to use the *in situ* generated solvent as the organic solvent in the pretreatment.

In various embodiments, the fluid phase digestion medium in which the hydrothermal digestion and catalytic reduction reaction, in the hydrothermal hydrocatalytic
30 reaction zone, are conducted may comprise an organic solvent and water. Although any organic solvent that is at least partially miscible with water may be used as a digestion solvent, particularly advantageous organic solvents are those that can be directly converted into fuel blends and other materials without being separated from the alcoholic component

being produced from the cellulosic biomass solids. That is, particularly advantageous organic solvents are those that may be co-processed along with the alcoholic component during downstream processing reactions into fuel blends and other materials. Suitable organic solvents in this regard may include, for example, ethanol, ethylene glycol, propylene glycol, glycerol, phenolics and any combination thereof. *In situ* generated organic solvents are particularly desirable in this regard.

In some embodiments, the fluid phase digestion medium may comprise between about 1% water and about 99% water. Although higher percentages of water may be more favorable from an environmental standpoint, higher quantities of organic solvent may more effectively promote hydrothermal digestion due to the organic solvent's greater propensity to solubilize carbohydrates and promote catalytic reduction of the soluble carbohydrates. In some embodiments, the fluid phase digestion medium may comprise about 90% or less water by weight. In other embodiments, the fluid phase digestion medium may comprise about 80% or less water by weight, or about 70% or less water by weight, or about 60% or less water by weight, or about 50% or less water by weight, or about 40% or less water by weight, or about 30% or less water by weight, or about 20% or less water by weight, or about 10% or less water by weight, or about 5% or less water by weight.

In some embodiments, catalysts capable of activating molecular hydrogen hydrothermal hydrocatalytic catalysts, which are capable of activating molecular hydrogen (e.g., hydrogenolysis catalyst) and conducting a catalytic reduction reaction may comprise a metal such as, for example, Cr, Mo, W, Re, Mn, Cu, Cd, Fe, Co, Ni, Pt, Pd, Rh, Ru, Ir, Os, and alloys or any combination thereof, either alone or with promoters such as Au, Ag, Cr, Zn, Mn, Sn, Bi, B, O, and alloys or any combination thereof. In some embodiments, the catalysts and promoters may allow for hydrogenation and hydrogenolysis reactions to occur at the same time or in succession of one another. In some embodiments, such catalysts may also comprise a carbonaceous pyropolymer catalyst containing transition metals (e.g., Cr, Mo, W, Re, Mn, Cu, and Cd) or Group VIII metals (e.g., Fe, Co, Ni, Pt, Pd, Rh, Ru, Ir, and Os). In some embodiments, the foregoing catalysts may be combined with an alkaline earth metal oxide or adhered to a catalytically active support. In some other embodiments, the catalyst may be deposited on a catalyst support that may not itself be catalytically active.

In some embodiments, the hydrothermal hydrocatalytic catalyst may comprise a slurry catalyst. In some embodiments, the slurry catalyst may comprise a poison-tolerant

catalyst. As used herein the term “poison-tolerant catalyst” refers to a catalyst that is capable of activating molecular hydrogen without needing to be regenerated or replaced due to low catalytic activity for at least about 12 hours of continuous operation. Use of a poison-tolerant catalyst may be particularly desirable when reacting soluble carbohydrates
5 derived from cellulosic biomass solids that have not had catalyst poisons removed therefrom. Catalysts that are not poison tolerant may also be used to achieve a similar result, but they may need to be regenerated or replaced more frequently than does a poison-tolerant catalyst.

In some embodiments, suitable poison-tolerant catalysts may include, for example,
10 sulfided catalysts. In some or other embodiments, nitrided catalysts may be used as poison-tolerant catalysts. Sulfided catalysts suitable for activating molecular hydrogen and buffers suitable for use with such catalysts are described in commonly owned United States Patent Application Publications US20120317872, US20130109896, and US20120317873, and United States Published Patent Application US20140166221. Sulfiding may take
15 place by treating the catalyst with hydrogen sulfide or an alternative sulfiding agent, optionally while the catalyst is disposed on a solid support. In more particular embodiments, the poison-tolerant catalyst may comprise (a) sulfur and (b) Mo or W and (c) Co and/or Ni or mixtures thereof. The pH buffering agent, may be suitable be an inorganic salt, particularly alkali salts such as, for example, potassium hydroxide, sodium hydroxide, and
20 potassium carbonate or ammonia. In other embodiments, catalysts containing Pt or Pd may also be effective poison-tolerant catalysts for use in the techniques described herein. When mediating *in situ* catalytic reduction reaction processes, sulfided catalysts may be particularly well suited to form reaction products comprising a substantial fraction of glycols (*e.g.*, C₂ – C₆ glycols) without producing excessive amounts of the corresponding
25 monohydric alcohols. Although poison-tolerant catalysts, particularly sulfided catalysts, may be well suited for forming glycols from soluble carbohydrates, it is to be recognized that other types of catalysts, which may not necessarily be poison-tolerant, may also be used to achieve a like result in alternative embodiments. As will be recognized by one having ordinary skill in the art, various reaction parameters (*e.g.*, temperature, pressure,
30 catalyst composition, introduction of other components, and the like) may be modified to favor the formation of a desired reaction product. Given the benefit of the present disclosure, one having ordinary skill in the art will be able to alter various reaction

parameters to change the product distribution obtained from a particular catalyst and set of reactants.

In some embodiments, slurry catalysts suitable for use in the methods described herein may be sulfided by dispersing a slurry catalyst in a fluid phase and adding a sulfiding agent thereto. Suitable sulfiding agents may include, for example, organic sulfoxides (*e.g.*, dimethyl sulfoxide), hydrogen sulfide, salts of hydrogen sulfide (*e.g.*, NaSH), and the like. In some embodiments, the slurry catalyst may be concentrated in the fluid phase after sulfiding, and the concentrated slurry may then be distributed in the cellulosic biomass solids using fluid flow. Illustrative techniques for catalyst sulfiding that may be used in conjunction with the methods described herein are described in United States Patent Application Publication US20100236988.

In various embodiments, slurry catalysts used in conjunction with the methods described herein may have a particulate size of about 250 microns or less. In some embodiments, the slurry catalyst may have a particulate size of about 100 microns or less, or about 10 microns or less. In some embodiments, the minimum particulate size of the slurry catalyst may be about 1 micron. In some embodiments, the slurry catalyst may comprise catalyst fines in the processes described herein.

Catalysts that are not particularly poison-tolerant may also be used in conjunction with the techniques described herein. Such catalysts may include, for example, Ru, Pt, Pd, or compounds thereof disposed on a solid support such as, for example, Ru on titanium dioxide or Ru on carbon. Although such catalysts may not have particular poison tolerance, they may be regenerable, such as through exposure of the catalyst to water at elevated temperatures, which may be in either a subcritical state or a supercritical state.

In some embodiments, the catalysts used in conjunction with the processes described herein may be operable to generate molecular hydrogen. For example, in some embodiments, catalysts suitable for aqueous phase reforming (*i.e.*, APR catalysts) may be used. Suitable APR catalysts may include, for example, catalysts comprising Pt, Pd, Ru, Ni, Co, or other Group VIII metals alloyed or modified with Re, Mo, Sn, or other metals such as described in United States Patent Publication US20080300435.

In some embodiments, the alcoholic component formed from the cellulosic biomass solids may be further reformed into a biofuel. Reforming the alcoholic component into a biofuel or other material may comprise any combination and sequence of further hydrogenolysis reactions and/or hydrogenation reactions, condensation reactions,

isomerization reactions, oligomerization reactions, hydrotreating reactions, alkylation reactions, dehydration reactions, desulfurization reactions, and the like. The subsequent conversion reactions may be catalytic or non-catalytic. In some embodiments, an initial operation of downstream conversion may comprise a condensation reaction, often
5 conducted in the presence of a condensation catalyst, in which the alcoholic component or a product derived therefrom is condensed with another molecule to form a higher molecular weight compound. As used herein, the term “condensation reaction” will refer to a chemical transformation in which two or more molecules are coupled with one another to form a carbon-carbon bond in a higher molecular weight compound, usually
10 accompanied by the loss of a small molecule such as water or an alcohol. An illustrative condensation reaction is the Aldol condensation reaction, which will be familiar to one having ordinary skill in the art. Additional disclosure regarding condensation reactions and catalysts suitable for promoting condensation reactions is provided hereinbelow.

In some embodiments, methods described herein may further comprise performing
15 a condensation reaction on the alcoholic component or a product derived therefrom. In various embodiments, the condensation reaction may take place at a temperature ranging between about 5°C and about 500°C. The condensation reaction may take place in a condensed phase (*e.g.*, a liquor phase) or in a vapor phase. For condensation reactions taking place in a vapor phase, the temperature may range between about 75°C and about
20 500°C, or between about 125°C and about 450°C. For condensation reactions taking place in a condensed phase, the temperature may range between about 5°C and about 475°C, or between about 15°C and about 300°C, or between about 20°C and about 250°C.

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.

In various embodiments, the higher molecular weight compound produced by the condensation reaction may comprise $\geq C_4$ hydrocarbons. In some or other embodiments,
30 the higher molecular weight compound produced by the condensation reaction may comprise $\geq C_6$ hydrocarbons. In some embodiments, the higher molecular weight compound produced by the condensation reaction may comprise $C_4 - C_{30}$ hydrocarbons. In some embodiments, the higher molecular weight compound produced by the

condensation reaction may comprise C₆ – C₃₀ hydrocarbons. In still other embodiments, the higher molecular weight compound produced by the condensation reaction may comprise C₄ – C₂₄ hydrocarbons, or C₆ – C₂₄ hydrocarbons, or C₄ – C₁₈ hydrocarbons, or C₆ – C₁₈ hydrocarbons, or C₄ – C₁₂ hydrocarbons, or C₆ – C₁₂ hydrocarbons. As used
5 herein, the term “hydrocarbons” refers to compounds containing both carbon and hydrogen without reference to other elements that may be present. Thus, heteroatom-substituted compounds are also described herein by the term “hydrocarbons.”

The particular composition of the higher molecular weight compound produced by the condensation reaction may vary depending on the catalyst(s) and temperatures used for
10 both the catalytic reduction reaction and the condensation reaction, as well as other parameters such as pressure.

In some embodiments, a single catalyst may mediate the transformation of the alcoholic component into a form suitable for undergoing a condensation reaction as well as mediating the condensation reaction itself. In other embodiments, a first catalyst may be
15 used to mediate the transformation of the alcoholic component into a form suitable for undergoing a condensation reaction, and a second catalyst may be used to mediate the condensation reaction. Unless otherwise specified, it is to be understood that reference herein to a condensation reaction and condensation catalyst refers to either type of condensation process. Further disclosure of suitable condensation catalysts now follows.

In some embodiments, a single catalyst may be used to form a higher molecular weight compound via a condensation reaction. Without being bound by any theory or mechanism, it is believed that such catalysts may mediate an initial dehydrogenation of the alcoholic component, followed by a condensation reaction of the dehydrogenated alcoholic component. Zeolite catalysts are one type of catalyst suitable for directly converting
20 alcohols to condensation products in such a manner. A particularly suitable zeolite catalyst in this regard may be ZSM-5, although other zeolite catalysts may also be suitable.

In some embodiments, two catalysts may be used to form a higher molecular weight compound via a condensation reaction. Without being bound by any theory or mechanism, it is believed that the first catalyst may mediate an initial dehydrogenation of
30 the alcoholic component, and the second catalyst may mediate a condensation reaction of the dehydrogenated alcoholic component. Like the single-catalyst embodiments discussed previously above, in some embodiments, zeolite catalysts may be used as either the first

catalyst or the second catalyst. Again, a particularly suitable zeolite catalyst in this regard may be ZSM-5, although other zeolite catalysts may also be suitable.

Various catalytic processes may be used to form higher molecular weight compounds by a condensation reaction. In some embodiments, the catalyst used for mediating a condensation reaction may comprise a basic site, or both an acidic site and a basic site. Catalysts comprising both an acidic site and a basic site will be referred to herein as multi-functional catalysts. In some or other embodiments, a catalyst used for mediating a condensation reaction may comprise one or more metal atoms. Any of the condensation catalysts may also optionally be disposed on a solid support, if desired.

10 In some embodiments, the condensation catalyst may comprise a basic catalyst comprising Li, Na, K, Cs, B, Rb, Mg, Ca, Sr, Si, Ba, Al, Zn, Ce, La, Y, Sc, Y, Zr, Ti, hydrotalcite, zinc-aluminate, phosphate, base-treated aluminosilicate zeolite, a basic resin, basic nitride, alloys or any combination thereof. In some embodiments, the basic catalyst may also comprise an oxide of Ti, Zr, V, Nb, Ta, Mo, Cr, W, Mn, Re, Al, Ga, In, Co, Ni,
15 Si, Cu, Zn, Sn, Cd, Mg, P, Fe, or any combination thereof. In some embodiments, the basic catalyst may comprise a mixed-oxide basic catalyst. Suitable mixed-oxide basic catalysts may comprise, for example, Si--Mg--O, Mg--Ti--O, Y--Mg--O, Y--Zr--O, Ti--Zr--O, Ce--Zr--O, Ce--Mg--O, Ca--Zr--O, La--Zr--O, B--Zr--O, La--Ti--O, B--Ti--O, and any combination thereof. In some embodiments, the condensation catalyst may further
20 include a metal or alloys comprising metals such as, for example, Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Bi, Pb, Os, alloys and combinations thereof. Use of metals in the condensation catalyst may be desirable when a dehydrogenation reaction is to be carried out in concert with the condensation reaction. Basic resins may include resins that exhibit basic functionality. The basic catalyst may be
25 self-supporting or adhered to a support containing a material such as, for example, carbon, silica, alumina, zirconia, titania, vanadia, ceria, nitride, boron nitride, a heteropolyacid, alloys and mixtures thereof.

In some embodiments, the condensation catalyst may comprise a hydrotalcite material derived from a combination of MgO and Al₂O₃. In some embodiments, the
30 condensation catalyst may comprise a zinc aluminate spinel formed from a combination of ZnO and Al₂O₃. In still other embodiments, the condensation catalyst may comprise a combination of ZnO, Al₂O₃, and CuO. Each of these materials may also contain an additional metal or alloy, including those more generally referenced above for basic

condensation catalysts. In more particular embodiments, the additional metal or alloy may comprise a Group 10 metal such Pd, Pt, or any combination thereof.

In some embodiments, the condensation catalyst may comprise a basic catalyst comprising a metal oxide containing, for example, Cu, Ni, Zn, V, Zr, or any mixture
5 thereof. In some or other embodiments, the condensation catalyst may comprise a zinc aluminate containing, for example, Pt, Pd, Cu, Ni, or any mixture thereof.

In some embodiments, the condensation catalyst may comprise a multi-functional catalyst having both an acidic functionality and a basic functionality. Such condensation catalysts may comprise a hydrotalcite, a zinc-aluminate, a phosphate, Li, Na, K, Cs, B, Rb,
10 Mg, Si, Ca, Sr, Ba, Al, Ce, La, Sc, Y, Zr, Ti, Zn, Cr, or any combination thereof. In further embodiments, the multi-functional catalyst may also include one or more oxides from the group of Ti, Zr, V, Nb, Ta, Mo, Cr, W, Mn, Re, Al, Ga, In, Fe, Co, Ir, Ni, Si, Cu, Zn, Sn, Cd, P, and any combination thereof. In some embodiments, the multi-functional catalyst may include a metal such as, for example, Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In,
15 Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, alloys or combinations thereof. The basic catalyst may be self-supporting or adhered to a support containing a material such as, for example, carbon, silica, alumina, zirconia, titania, vanadia, ceria, nitride, boron nitride, a heteropolyacid, alloys and mixtures thereof.

In some embodiments, the condensation catalyst may comprise a metal oxide
20 containing Pd, Pt, Cu or Ni. In still other embodiments, the condensation catalyst may comprise an aluminate or a zirconium metal oxide containing Mg and Cu, Pt, Pd or Ni. In still other embodiments, a multi-functional catalyst may comprise a hydroxyapatite (HAP) combined with one or more of the above metals.

In some embodiments, the condensation catalyst may also include a zeolite and
25 other microporous supports that contain Group IA compounds, such as Li, Na, K, Cs and Rb. Preferably, the Group IA material may be present in an amount less than that required to neutralize the acidic nature of the support. A metal function may also be provided by the addition of group VIIIB metals, or Cu, Ga, In, Zn or Sn. In some embodiments, the condensation catalyst may be derived from the combination of MgO and Al₂O₃ to form a
30 hydrotalcite material. Another condensation catalyst may comprise a combination of MgO and ZrO₂, or a combination of ZnO and Al₂O₃. Each of these materials may also contain an additional metal function provided by copper or a Group VIIIB metal, such as Ni, Pd, Pt, or combinations of the foregoing.

The condensation reaction mediated by the condensation catalyst may be carried out in any reactor of suitable design, including continuous-flow, batch, semi-batch or multi-system reactors, without limitation as to design, size, geometry, flow rates, and the like. The reactor system may also use a fluidized catalytic bed system, a swing bed
5 system, fixed bed system, a moving bed system, or a combination of the above. In some embodiments, bi-phasic (*e.g.*, liquid-liquid) and tri-phasic (*e.g.*, liquid-liquid-solid) reactors may be used to carry out the condensation reaction.

In some embodiments, an acid catalyst may be used to optionally dehydrate at least a portion of the reaction product. Suitable acid catalysts for use in the dehydration reaction
10 may include, but are not limited to, mineral acids (*e.g.*, HCl, H₂SO₄), solid acids (*e.g.*, zeolites, ion-exchange resins) and acid salts (*e.g.*, LaCl₃). Additional acid catalysts may include, without limitation, zeolites, carbides, nitrides, zirconia, alumina, silica, aluminosilicates, phosphates, titanium oxides, zinc oxides, vanadium oxides, lanthanum
15 oxides, yttrium oxides, scandium oxides, magnesium oxides, cerium oxides, barium oxides, calcium oxides, hydroxides, heteropolyacids, inorganic acids, acid modified resins, base modified resins, and any combination thereof. In some embodiments, the dehydration catalyst may also include a modifier. Suitable modifiers may include, for example, La, Y, Sc, P, B, Bi, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, and any combination thereof. The
20 modifiers may be useful, *inter alia*, to carry out a concerted hydrogenation/dehydrogenation reaction with the dehydration reaction. In some embodiments, the dehydration catalyst may also include a metal. Suitable metals may include, for example, Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, alloys, and any combination thereof. The dehydration catalyst may be self-supporting, supported on an inert support or resin, or it may be dissolved in a fluid.

25 Various operations may optionally be performed on the alcoholic component prior to conducting a condensation reaction. In addition, various operations may optionally be performed on a fluid phase containing the alcoholic component, thereby further transforming the alcoholic component or placing the alcoholic component in a form more suitable for taking part in a condensation reaction. These optional operations are now
30 described in more detail below.

As described above, one or more liquid phases may be present when digesting cellulosic biomass solids. Particularly when cellulosic biomass solids are fed continuously or semi-continuously to the hydrothermal (hydrocatalytic) digestion unit, digestion of the

cellulosic biomass solids may produce multiple liquid phases in the hydrothermal digestion unit. The liquid phases may be immiscible with one another, or they may be at least partially miscible with one another. In some embodiments, the one or more liquid phases may comprise a phenolics liquid phase comprising lignin or a product formed therefrom, an aqueous phase comprising the alcoholic component, a light organics phase, or any combination thereof. The alcoholic component being produced from the cellulosic biomass solids may be partitioned between the one or more liquid phases, or the alcoholic component may be located substantially in a single liquid phase. For example, the alcoholic component being produced from the cellulosic biomass solids may be located predominantly in an aqueous phase (*e.g.*, an aqueous phase digestion solvent), although minor amounts of the alcoholic component may be partitioned to the phenolics liquid phase or a light organics phase. In various embodiments, the slurry catalyst may accumulate in the phenolics liquid phase as it forms, thereby complicating the return of the slurry catalyst to the cellulosic biomass solids in the manner described above. Alternative configurations for distributing slurry catalyst particulates in the cellulosic biomass solids when excessive catalyst accumulation in the phenolics liquid phase has occurred are described hereinafter.

Accumulation of the slurry catalyst in the phenolics liquid phase may, in some embodiments, be addressed by conveying this phase and the accumulated slurry catalyst therein to the same location where a fluid phase digestion medium is being contacted with cellulosic biomass solids. The fluid phase digestion medium and the phenolics liquid phase may be conveyed to the cellulosic biomass solids together or separately. Thusly, either the fluid phase digestion medium and/or the phenolics liquid phase may motively return the slurry catalyst back to the cellulosic biomass solids such that continued stabilization of soluble carbohydrates may take place. In some embodiments, at least a portion of the lignin in the phenolics liquid phase may be depolymerized before or while conveying the phenolics liquid phase for redistribution of the slurry catalyst. At least partial depolymerization of the lignin in the phenolics liquid phase may reduce the viscosity of this phase and make it easier to convey. Lignin depolymerization may take place chemically by hydrolyzing the lignin (*e.g.*, with a base) or thermally by heating the lignin to a temperature of at least about 250°C in the presence of molecular hydrogen and the slurry catalyst. Further details regarding lignin depolymerization and the use of viscosity monitoring as a means of process control are described in commonly owned United States Patent Application 61/720765, filed October 31, 2012.

After forming the alcoholic component from the cellulosic biomass solids, at least a portion of the alcoholic component may be separated from the cellulosic biomass solids and further processed by performing a condensation reaction thereon, as generally described above. Processing of the alcoholic component that has partitioned between
5 various liquid phases may take place with the phases separated from one another, or with the liquid phases mixed together. For example, in some embodiments, the alcoholic component in a fluid phase digestion medium may be processed separately from a light organics phase. In other embodiments, the light organics phase may be processed concurrently with the fluid phase digestion medium.

10 Optionally, the fluid phase digestion medium containing the alcoholic component may be subjected to a second catalytic reduction reaction external to the cellulosic biomass solids, if needed, for example, to increase the amount of soluble carbohydrates that are converted into the alcoholic component and/or to further reduce the degree of oxygenation of the alcoholic components that are formed. For example, in some embodiments, a glycol
15 or more highly oxygenated alcohol may be transformed into a monohydric alcohol by performing a second catalytic reduction reaction. The choice of whether to perform a condensation reaction on a monohydric alcohol or a glycol may be based on a number of factors, as discussed in more detail below, and each approach may present particular advantages.

20 In some embodiments, a glycol produced from the cellulosic biomass solids may be fed to the condensation catalyst. Although glycols may be prone to coking when used in conjunction with condensation catalysts, particularly zeolite catalysts, the present inventors found the degree of coking to be manageable in the production of higher molecular weight compounds. Approaches for producing glycols from cellulosic biomass solids and feeding
25 the glycols to a condensation catalyst are described in commonly owned United States Published Patent Application US20140121420.

In some embodiments, a phenolics liquid phase formed from the cellulosic biomass solids may be further processed. Processing of the phenolics liquid phase may facilitate the catalytic reduction reaction being performed to stabilize soluble carbohydrates. In
30 addition, further processing of the phenolics liquid phase may be coupled with the production of dried glycols or dried monohydric alcohols for feeding to a condensation catalyst. Moreover, further processing of the phenolics liquid phase may produce methanol and phenolic compounds from degradation of the lignin present in the cellulosic

biomass solids, thereby increasing the overall weight percentage of the cellulosic biomass solids that may be transformed into useful materials. Finally, further processing of the phenolics liquid phase may improve the lifetime of the slurry catalyst.

5 These liquid phases or fluid phases can be used to remove water in the pretreatment as organic solvent, in the third contact zone, and thus be available for further processing.

10 Various techniques for processing a phenolics liquid phase produced from cellulosic biomass solids are described in commonly owned United States Published Patent Applications US20140121419, US20140117277, and US20140121418. As described therein, in some embodiments, the viscosity of the phenolics liquid phase may be reduced in order to facilitate conveyance or handling of the phenolics liquid phase. As further described therein, deviscosification of the phenolics liquid phase may take place by chemically hydrolyzing the lignin and/or heating the phenolics liquid phase in the presence of molecular hydrogen (*i.e.*, hydrotreating) to depolymerize at least a portion of the lignin present therein in the presence of accumulated slurry catalyst. Deviscosification of the phenolics liquid phase may take place before or after separation of the phenolics liquid phase from one or more of the other liquid phases present, and thermal deviscosification may be coupled to the reaction or series of reactions used to produce the alcoholic component from the cellulosic biomass solids. Moreover, after deviscosification of the phenolics liquid phase, the slurry catalyst may be removed therefrom. The catalyst may then be regenerated, returned to the cellulosic biomass solids, or any combination thereof.

15 In some embodiments, heating of the cellulosic biomass solids and the fluid phase digestion medium to form soluble carbohydrates and a phenolics liquid phase may take place while the cellulosic biomass solids are in a pressurized state. As used herein, the term “pressurized state” refers to a pressure that is greater than atmospheric pressure (1 bar). Heating a fluid phase digestion medium in a pressurized state may allow the normal boiling point of the digestion solvent to be exceeded, thereby allowing the rate of hydrothermal digestion to be increased relative to lower temperature digestion processes. In some embodiments, heating the cellulosic biomass solids and the fluid phase digestion medium may take place at a pressure of at least about 30 bar. In some embodiments, heating the cellulosic biomass solids and the fluid phase digestion medium may take place at a pressure of at least about 60 bar, or at a pressure of at least about 90 bar. In some embodiments, heating the cellulosic biomass solids and the fluid phase digestion medium may take place at a pressure ranging between about 30 bar and about 430 bar. In some

embodiments, heating the cellulosic biomass solids and the fluid phase digestion medium may take place at a pressure ranging between about 50 bar and about 330 bar, or at a pressure ranging between about 70 bar and about 130 bar, or at a pressure ranging between about 30 bar and about 130 bar.

- 5 To facilitate a better understanding of the present invention, the following examples of preferred embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

ILLUSTRATIVE EXAMPLES

Examples1-5: Base Wash

- 10 A series of biomass pretreatment experiments were conducted in 15-mm or 25-mm diameter glass chromatography columns (Ace Glassware), with pretreatment solutions fed from glass buret via a Low-Flow Compact Metering Pump, 30 mL/min maximum, 115 VAC, from Cole Parmer (WU-07115-10). A retriever 500 fraction collector from Isco / Teledyne was used to collect sample fractions. Southeastern US pine wood was ground to
15 a dimension of approximately 8-mm x 3-mm x 3-mm using a “Retsch Grinder” Model SM100 is a rotating knife blade grinder.

- Samples of the feed wood, and wood following treatment were analyzed for metals via combustion, then dissolution of the resulting ash in sulfuric acid for analysis by plasma emission spectroscopy. A second sample was analyzed by ion chromatography to
20 determine the chloride content of the wood samples.

Treatments for the biomass wash sequence entailed use of 0.5N KOH, deionized water, and 25% ethanol in deionized water.

- The volume of the bed of wood treated was determined from the known column diameter, and the measured length of the wood bed, which was retained either via
25 adjustable plungers, or silane treated glass wool plugs. Packing density for the ground wood samples ranged from 0.21 to 0.25 dry grams per milliliter of bed volume.

Results of the treatment experiments are tabulated in Table 1.

Table 1: Biomass pretreatment experiments

Parameter	Units	Ex-1	Ex-2	Ex-3	Ex-4	Ex-5
Flowrate	BV/h	0.71	0.46	0.62	0.78	0.73
1% H ₂ SO ₄	BV	0.00	0.28	0.99	0.14	0.00
0.5N KOH	BV	0	0	0.99	0.14	0.26
DI Water	BV	3.39	2.20	0.99	2.48	2.33
25% EtOH	BV	0.00	0.00	1.98	0.00	0.00
Total BV	BV	3.39	2.48	4.95	2.76	2.59
Phosphorus	% remove	32.2%	22.0%	100.0%	100.0%	100.0%
Manganese	% remove	-6.5%	90.3%	96.8%	71.0%	-9.7%
Iron	% remove	73.9%	78.3%	91.3%	87.0%	91.3%
Magnesium	% remove	26.8%	92.9%	98.4%	85.0%	37.8%
Calcium	% remove	48.1%	92.9%	98.3%	86.9%	51.9%
Chloride	% remove	54.5%	72.7%	80.0%	85.5%	83.6%

5

Comparison of Examples 1 and 2 where no base was used, vs. the other examples shows that base is important for removal of the chlorine and phosphorus, which are presumed to be ion exchanged into the wood matrix. The amount of base used to treat the wood could be very small, followed by waster wash to flush the base zone through the bed. Base addition was effective in removing phosphorous and improved the removal of chloride, as evidence in Examples 3 through 5.

Example 6: Solvent Drying

15 A 15-mm inside diameter x 24 inch glass chromatography column was charged with 23 inches of ground pine wood with moisture content of 52.4%, measured by drying of a sample in a vacuum oven overnight at 86 °C. 39.6 grams of wood were charged. Ethanol (less than 1000 ppm H₂O) was charged as solvent to a feed buret. The solvent was flowed upflow through the column at 0.8 ml/min using a Low-Flow Compact Metering Pump, 30 mL/min maximum, 115 VAC, from Cole Parmer (WU-07115-10). A retriever 500 fraction collector from Isco / Teledyne was used to collect sample fractions. Southeastern US pine wood was ground to a dimension of approximately 8-mm x 3-mm x 3-mm using a “Retsch Grinder” Model SM100 is a rotating knife blade grinder.

25 Samples were collected in 50-ml fractions (0.48 bed volumes [BV]), and analyzed by Karl Fisher titration for water content. At the end of 3.9 bed volumes of solvent wash, the cumulative water removed corresponded to 103% of the assessed water content of the

initially charged wood. This result indicates virtual complete removal of water via use of ethanol as solvent, under the conditions described.

Example 7: Gas displacement

- 5 A 15-mm glass chromatography column was packed to a bed length of 22.5 inches with ground wood. The column was subjected to 1% sulfuric acid, water, and 0.5N base wash, followed by a final water rinse. Approximately 60 ml of final aqueous phase was drained from the bed at the end of the treatment sequence, representing 59% of the total bed volume.
- 10 This example represents draining of interstitial liquid from a water-wet bed, to remove a substantial (greater than 50%) portion of the liquid used to push base wash through the bed. The drained water can be re-used for subsequent wash steps.

C L A I M S

1. A method for selective removal of chlorine and phosphorus from a cellulosic biomass solids comprising:
 - a. providing a detrimental species-containing cellulosic biomass solids;
 - b. introducing said detrimental species-containing cellulosic biomass solids
5 from an inlet into a treatment vessel, said cellulosic biomass solids having a true interstitial volume in said vessel;
 - c. introducing a base solution having a pH of greater than 9 from an inlet to said cellulosic biomass solids containing vessel at a temperature in the range of 0°C to 60°C in an amount to fill at least about 5% bed volume to at most
10 about 40% bed volume of said true interstitial volume;
 - d. subsequently to step c, introducing an aqueous solution having a pH of at most 8 from an inlet to said basic cellulosic biomass solids-containing vessel, thereby producing washed cellulosic biomass solids having reduced detrimental species content compared to the detrimental species-containing
15 cellulosic biomass solids and a basic water effluent, wherein said basic water effluent is in the range of about 3 parts to about 0.5 parts relative to about 1 part of detrimental species-containing cellulosic biomass solids (dry basis);
 - e. introducing a removal stream comprising a gas stream or an organic solvent
20 solution from an inlet to the vessel containing the washed cellulosic biomass solids thereby producing a pretreated cellulosic biomass solids with reduced water content compared to the water washed cellulosic biomass solids and an aqueous effluent;
 - f. discharging the pretreated cellulosic biomass solids from an outlet and
25 transferring at least a portion of the discharged pretreated biomass solids to a digestion and/or reaction zone;
 - g. recycling at least a first portion of the aqueous effluent to produce base solution; and
 - h. recycling at least a second portion of the aqueous effluent as an aqueous
30 solution.

2. A method according to claim 1, wherein the base solution comprises a base selected from sodium hydroxide, potassium hydroxide or ammonia.
3. A method according to claims 1 or 2, wherein the base solution comprises a base in an amount of less than 5 Normal and at least 0.01 Normal
4. A method according to any of claims 1 to 3, wherein the organic solvent is a solvent used in the digestion and/or reaction zone.
- 5 5. A method according any of claims 1 to 4, wherein, in the digestion and/or reaction zone, the treated cellulosic biomass is contacted with a hydrothermal hydrocatalytic catalyst in the presence of hydrogen in the presence of a digestion solvent thereby producing an intermediate oxygenated product stream; at least a portion of the oxygenated intermediate product stream is converted to a hydrocarbon product stream comprising hydrocarbons and water; and at least a portion of the water is separated and recycled to form at least a portion of the aqueous solution.
- 10 6. A method according to any of claims 1 to 4, wherein, in the digestion and/or reaction zone, the treated cellulosic biomass is contacted with a hydrothermal hydrocatalytic catalyst in the presence of hydrogen in the presence of a digestion solvent thereby producing an intermediate oxygenated product stream; at least a portion of the oxygenated intermediate product stream is converted to a hydrocarbon product stream comprising hydrocarbons and water; and at least a portion of the water is separated and recycled to form at least a portion of the aqueous solution.
- 15 7. A method according to claim 6, wherein, the oxygenated intermediate product steam comprises oxygenated hydrocarbons and water, and at least a portion of the water is separated and recycled form at least a portion of the aqueous solution.
- 20 8. A method according to any of claims 1 to 7, wherein the loss of carbohydrate from the washing is less than 10% by weight, based on the carbohydrates present in the biomass (dry basis).
- 25

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/071043

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10G1/06 C10G3/00 C07G1/00 C08L1/02
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C10G C07G C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/317873 A1 (JOHNSON KIMBERLY ANN [US] ET AL) 20 December 2012 (2012-12-20) cited in the application paragraphs [0009], [0021] - [0022], [0025] - [0037] -----	1-8
A	WO 2013/120492 A1 (INBICON AS [DK]) 22 August 2013 (2013-08-22) page 5 - page 11 -----	1-8
A	US 2012/152836 A1 (POWELL JOSEPH BROUN [US] ET AL) 21 June 2012 (2012-06-21) examples 6-11 -----	1-8
A	US 2012/151827 A1 (POWELL JOSEPH BROUN [US] ET AL) 21 June 2012 (2012-06-21) example 2; table 1 -----	1-8

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search
 24 March 2015

Date of mailing of the international search report
 30/03/2015

Name and mailing address of the ISA/
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer
 Bernet, Olivier

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/071043

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2012317873	A1	20-12-2012	CA 2839069 A1	20-12-2012
			CA 2839186 A1	20-12-2012
			CN 103608439 A	26-02-2014
			CN 103620002 A	05-03-2014
			EP 2721124 A1	23-04-2014
			EP 2721125 A1	23-04-2014
			US 2012317872 A1	20-12-2012
			US 2012317873 A1	20-12-2012
			WO 2012174088 A1	20-12-2012
			WO 2012174103 A1	20-12-2012

WO 2013120492	A1	22-08-2013	AU 2013220805 A1	04-09-2014
			CA 2863978 A1	22-08-2013
			CN 104066847 A	24-09-2014
			EA 201491392 A1	30-01-2015
			EP 2814974 A1	24-12-2014
			KR 20140143142 A	15-12-2014
			WO 2013120492 A1	22-08-2013

US 2012152836	A1	21-06-2012	AU 2011349336 A1	11-07-2013
			CA 2822105 A1	28-06-2012
			CN 103347984 A	09-10-2013
			EP 2655557 A2	30-10-2013
			US 2012152836 A1	21-06-2012
			WO 2012088121 A2	28-06-2012

US 2012151827	A1	21-06-2012	AU 2011349254 A1	11-07-2013
			CA 2822084 A1	28-06-2012
			CN 103415592 A	27-11-2013
			EP 2655558 A2	30-10-2013
			US 2012151827 A1	21-06-2012
			WO 2012088131 A2	28-06-2012
