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(54) **BIOMASS CONVERSION SYSTEMS
PROVIDING INTEGRATED STABILIZATION
OF A HYDROLYSATE USING A SLURRY
CATALYST AND METHODS FOR USE
THEREOF**

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(57) **ABSTRACT**

Digestion of cellulosic biomass solids to form a hydrolysate may be conducted with integrated catalytic reduction during digestion to transform soluble carbohydrates in the hydrolysate into a more stable reaction product. Such integrated catalytic reduction may be conducted using a slurry catalyst. Biomass conversion systems for performing integrated catalytic reduction can comprise: a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular hydrogen; an optional hydrogen feed line that is operatively connected to the hydrothermal digestion unit; and a fluid circulation loop comprising the hydrothermal digestion unit and a catalytic reduction reactor unit, the catalytic reduction reactor unit also containing the slurry catalyst.

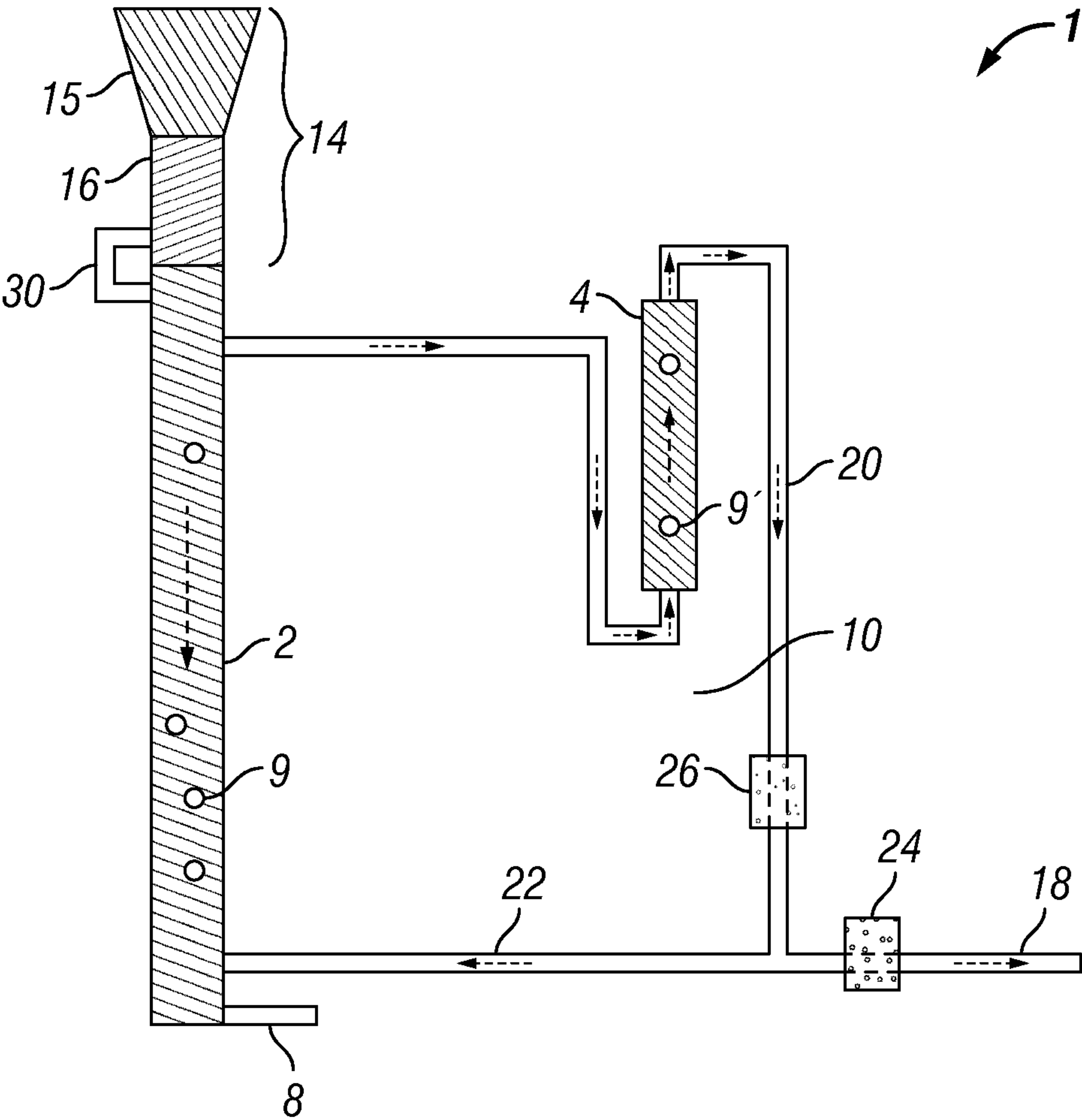


FIG. 1

**BIOMASS CONVERSION SYSTEMS
PROVIDING INTEGRATED STABILIZATION
OF A HYDROLYSATE USING A SLURRY
CATALYST AND METHODS FOR USE
THEREOF**

CROSS-REFERENCE TO RELATED
APPLICATION

[0001] This present application claims the benefit of U.S. Patent Application No. 61/665,641, filed Jun. 28, 2012, the entire disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present disclosure generally relates to the processing of cellulosic biomass solids using digestion to produce a hydrolysate, and, more specifically, to biomass conversion systems and methods for use thereof that allow a hydrolysate comprising soluble carbohydrates to be stabilized during digestion through use of a slurry catalyst.

BACKGROUND OF THE INVENTION

[0003] A number of substances of commercial significance may be produced from natural sources, particularly biomass. Cellulosic biomass may be particularly advantageous in this regard due to the versatility of the abundant carbohydrates found therein in various forms. As used herein, the term “cellulosic biomass” refers to a living or recently living biological material that contains cellulose. The lignocellulosic material found in the cell walls of higher plants is the world’s most abundant source of carbohydrates. Materials commonly produced from cellulosic biomass may include, for example, paper and pulpwood via partial digestion, and bioethanol by fermentation.

[0004] Plant cell walls are divided into two sections: primary cell walls and secondary cell walls. The primary cell wall provides structural support for expanding cells and contains 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 that is covalently crosslinked to hemicellulose. Hemicellulose and pectin are typically found in abundance, but cellulose is the predominant polysaccharide and the most abundant source of carbohydrates. The complex mixture of constituents that are co-present with the cellulose can make its processing difficult, as discussed hereinafter.

[0005] Significant attention has been placed on developing fossil fuel alternatives derived from renewable resources. Cellulosic biomass has garnered particular attention in this regard due to its abundance and the versatility of the various constituents found therein, particularly cellulose and other carbohydrates. Despite promise and intense interest, the development and implementation of bio-based fuel technology has been slow. Existing technologies have heretofore produced fuels having a low energy density (e.g., bioethanol) and/or that are not fully compatible with existing engine designs and transportation infrastructure (e.g., methanol, biodiesel, Fischer-Tropsch diesel, hydrogen, and methane). An energy- and cost-efficient process for processing cellulo-

sic biomass into fuel blends having similar compositions to fossil fuels would be highly desirable to address the foregoing issues and others.

[0006] When converting cellulosic biomass into fuel blends and other materials, cellulose and other complex carbohydrates therein can be extracted and transformed into simpler organic molecules, which can be further reformed thereafter. Fermentation is one process whereby complex carbohydrates from biomass may be converted into a more usable form. However, fermentation processes are typically slow, require large volume reactors, and produce an initial reaction product having a low energy density (ethanol). Digestion is another way in which cellulose and other complex carbohydrates may be converted into a more usable form. Digestion processes can break down cellulose and other complex carbohydrates within cellulosic biomass into simpler, soluble carbohydrates that are suitable for further transformation through downstream reforming reactions. 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. This basic requirement leads to a number of secondary issues that collectively present an immense engineering challenge that has not been solved heretofore.

[0007] The issues associated with converting cellulosic biomass into fuel blends in an energy- and cost-efficient manner using digestion are not only complex, but they are entirely different than those that are encountered in the digestion processes commonly used in the paper and pulpwood industry. Since the intent of cellulosic biomass digestion in the paper and pulpwood industry is to retain a solid material (e.g., wood pulp), incomplete digestion is usually performed at low temperatures (e.g., less than about 100° C.) for a fairly short period of time. In contrast, digestion processes suitable for converting cellulosic biomass into fuel blends and other materials are ideally configured to maximize yields by solubilizing as much of the original cellulosic biomass charge as possible in a high-throughput manner.

[0008] Production of greater quantities of soluble carbohydrates for use in fuel blends and other materials via routine modification of paper and pulpwood digestion processes is not feasible for a number of reasons. Simply running the digestion processes of the paper and pulpwood industry for a longer period of time to produce more soluble carbohydrates is undesirable from a throughput standpoint. Use of digestion promoters such as strong alkalis, strong acids, or sulfites to accelerate the digestion rate can increase process costs and complexity due to post-processing separation steps and the possible need to protect downstream components from these agents. Accelerating the digestion rate by increasing the digestion temperature can actually reduce yields due to thermal degradation of soluble carbohydrates that can occur at elevated digestion temperatures. Once produced by digestion, soluble carbohydrates are very reactive and can rapidly

degrade, especially under higher temperature conditions (e.g., above about 100° C., particularly above about 150° C.). Use of higher digestion temperatures can also be undesirable from an energy efficiency standpoint. Any of these difficulties can defeat the economic viability of fuel blends derived from cellulosic biomass.

[0009] One way in which soluble carbohydrates within a hydrolysate can be protected from thermal degradation is through subjecting them to a catalytic reduction reaction process, which may include hydrogenation and/or hydrogenolysis reactions. Stabilizing soluble carbohydrates within a hydrolysate through conducting one or more catalytic reduction reactions may allow digestion of cellulosic biomass to take place at higher temperatures than would otherwise be possible without unduly sacrificing yields. In addition, the products of a catalytic reduction reaction process may be readily transformable into fuel blends and other materials through downstream reforming reactions.

[0010] Another issue associated with the processing of cellulosic biomass into fuel blends is created by the need for high conversion percentages of a cellulosic biomass charge into soluble carbohydrates. Specifically, as cellulosic biomass solids are digested, their size eventually decreases to the point that they become fluidly mobile. As used herein, cellulosic biomass solids that are fluidly mobile, particularly cellulosic biomass solids that are about 3 mm in size or less, will be referred to as “cellulosic biomass fines.” Cellulosic biomass fines can be transported out of a digestion zone of a system for converting cellulosic biomass and into one or more zones where solids are unwanted and can be detrimental. For example, cellulosic biomass fines have the potential to plug catalyst beds, transfer lines, and the like. Furthermore, although small in size, cellulosic biomass fines may represent a non-trivial fraction of the cellulosic biomass charge, and if they are not further converted into soluble carbohydrates, the ability to attain a satisfactory conversion percentage may be impacted. Since the digestion processes of the paper and pulpwood industry are run at relatively low cellulosic biomass conversion percentages, smaller amounts of cellulosic biomass fines are believed to be generated and have a lesser impact on those digestion processes.

[0011] In addition to the desired carbohydrates, other materials may be present within cellulosic biomass that can be especially problematic to deal with in an energy- and cost-efficient manner. Sulfur- and/or nitrogen-containing amino acids or other catalyst poisons may be present in cellulosic biomass. If not removed, these catalyst poisons can impact the catalytic reduction reaction(s) used to stabilize soluble carbohydrates, thereby resulting in process downtime for catalyst regeneration and/or replacement and reducing the overall energy efficiency when restarting the process. On the other hand, in-process removal of these catalyst poisons can also impact the energy efficiency of the biomass conversion process, since the ion-exchange processes typically needed to affect their removal are usually conducted at temperatures below those at which soluble carbohydrates are produced by digestion, thereby introducing heat exchange operations that add to design complexity and may increase operational costs.

[0012] As evidenced by the foregoing, the efficient conversion of cellulosic biomass into fuel blends is a complex problem that presents immense engineering challenges. The present disclosure addresses these challenges and provides related advantages as well.

SUMMARY OF THE INVENTION

[0013] The present disclosure generally relates to the processing of cellulosic biomass solids using digestion to produce a hydrolysate, and, more specifically, to biomass conversion systems and methods for use thereof that allow a hydrolysate comprising soluble carbohydrates to be stabilized during digestion through use of a slurry catalyst.

[0014] In some embodiments, the present invention provides biomass conversion systems comprising: a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular hydrogen (“molecular hydrogen activating slurry catalyst”); an optional hydrogen feed line that is operatively connected to the hydrothermal digestion unit; and a fluid circulation loop comprising the hydrothermal digestion unit and a catalytic reduction reactor unit, the catalytic reduction reactor unit also containing the slurry catalyst.

[0015] In some embodiments, the present invention provides methods comprising: providing cellulosic biomass solids in a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular hydrogen (“molecular hydrogen activating slurry catalyst”); heating the cellulosic biomass solids in the hydrothermal digestion unit in the presence of molecular hydrogen while circulating the slurry catalyst therethrough, thereby forming a hydrolysate comprising soluble carbohydrates within a liquor phase; at least partially transforming the soluble carbohydrates into a reaction product while the soluble carbohydrates are within the hydrothermal digestion unit; and transferring at least a portion of the liquor phase to a catalytic reduction reactor unit that also contains the slurry catalyst, so as to further transform the soluble carbohydrates into the reaction product.

[0016] The features and advantages of the present disclosure will be readily apparent to one having ordinary skill in the art upon a reading of the description of the preferred embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWING

[0017] The following figure is included to illustrate certain aspects of the present disclosure, and should not be viewed as an exclusive embodiment. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to one having ordinary in the art and the benefit of this disclosure.

[0018] FIG. 1 shows a schematic of an illustrative biomass conversion system having a hydrothermal digestion unit and a catalytic reduction reactor unit coupled to one another in a fluid circulation loop, where both the hydrothermal digestion unit and the catalytic reduction reactor unit contain a slurry catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The present disclosure generally relates to the processing of cellulosic biomass solids using digestion to produce a hydrolysate, and, more specifically, to biomass conversion systems and methods for use thereof that allow a hydrolysate comprising soluble carbohydrates to be stabilized during digestion through use of a slurry catalyst.

[0020] In the embodiments described herein, the digestion rate of cellulosic biomass solids may be accelerated in the presence of a digestion solvent. In some instances, the digestion solvent may be maintained at elevated pressures that keep the digestion solvent in a liquid state above its normal boiling

point. Although the more rapid digestion rate of cellulosic biomass solids under these types of conditions may be desirable from the standpoint of throughput, soluble carbohydrates may be susceptible to degradation at elevated temperatures, as discussed above.

[0021] To combat the problems associated with degradation of soluble carbohydrates, the present disclosure provides systems and methods for digesting cellulosic biomass solids while effectively promoting the thermal stabilization of soluble carbohydrates produced therefrom. Specifically, the present disclosure provides systems and methods whereby hydrothermal digestion and one or more catalytic reduction reactions take place in the same vessel. We have found that stabilization of soluble carbohydrates occurs most effectively if conducted in this manner. The foregoing may be accomplished by including a slurry catalyst capable of activating molecular hydrogen within a hydrothermal digestion unit containing cellulosic biomass solids. As used herein, the term “slurry catalyst” refers to a catalyst comprising fluidly mobile catalyst particles that can be at least partially suspended in a fluid phase via gas flow, liquid flow, mechanical agitation, or any combination thereof. The presence of the slurry catalyst within the hydrothermal digestion unit may allow one or more in situ (integrated) catalytic reduction reactions to take place therein, thereby advantageously intercepting and transforming soluble carbohydrates into a more stable reaction product as soon as feasible after the soluble carbohydrates form. As used herein, the term “in situ catalytic reduction reaction” refers to a catalytic reduction reaction that occurs in the same vessel as a digestion process. Formation of the reaction product may reduce the amount of thermal decomposition that occurs during hydrothermal digestion, thereby enabling high yield conversion of cellulosic biomass solids into a desired reaction product to take place in a timely manner.

[0022] In addition to rapidly stabilizing soluble carbohydrates as a reaction product, conducting one or more in situ catalytic reduction reactions may also be particularly advantageous from an energy efficiency standpoint. Specifically, the hydrothermal digestion of cellulosic biomass is an endothermic process, whereas catalytic reduction reactions are exothermic. Thus, the excess heat generated by the in situ catalytic reduction reaction(s) may be utilized to drive the hydrothermal digestion, thereby lowering the amount of additional heat energy input needed to conduct digestion. Since digestion and catalytic reduction take place within the same vessel in the embodiments described herein, there is minimal opportunity for heat transfer loss to take place, as would occur if the catalytic reduction reaction(s) were to be conducted in a separate location. In addition, in such a configuration, the in situ catalytic reduction reaction(s) may provide a growing supply of the reaction product within the hydrothermal digestion unit, which may serve as and/or replenish the digestion solvent. Since the reaction product and the digestion solvent may be the same, there is no express need to separate and recycle a majority of the digestion solvent before further processing the reaction product downstream, which may be further advantageous from an energy efficiency standpoint.

[0023] Although conducting one or more in situ catalytic reduction reactions can be highly desirable for the purposes of stabilizing soluble carbohydrates and achieving heat integration, the catalyst poisons and other substances within cellulosic biomass may make implementing such a process very difficult. When conducting an in situ catalytic reduction reaction, there is no opportunity to remove catalyst poisons before

they contact the distributed slurry catalyst. One way in which this issue can be addressed is to use a poison-tolerant slurry catalyst, some of which are discussed hereinbelow. Another alternative is to use a slurry catalyst that is regenerable upon exposure to conditions that can be readily established in or near the hydrothermal digestion unit. For example, in some embodiments, a regenerable slurry catalyst may be regenerated through exposure to water at a temperature of at least about 300° C.

[0024] Once the soluble carbohydrates have been at least partially transformed into a more stable reaction product during hydrothermal digestion, completion of the conversion of the soluble carbohydrates into the reaction product may take place in a separate catalytic reduction reactor unit that also employs the slurry catalyst or a different catalyst that is capable of activating molecular hydrogen. The transformation that takes place in the catalytic reduction reactor unit may comprise a further reduction in the degree of oxidation of the initial reaction product, an increased conversion of soluble carbohydrates into oxygenated intermediates, or both. As used herein, the term “oxygenated intermediates” refers to alcohols, polyols, ketones, aldehydes, and mixtures thereof that are produced from a catalytic reduction reaction of soluble carbohydrates. The described biomass conversion system features can allow a significant quantity of the initially solubilized carbohydrates to be converted into a form that is suitable for subsequent processing into a biofuel, while forming as small as possible an amount of caramelans and other decomposition products in or near the hydrothermal digestion unit.

[0025] The reaction product obtained from the catalytic reduction reactor unit may be recirculated to the hydrothermal digestion unit, where it may serve as a digestion solvent, and/or be withdrawn from the catalytic reduction reactor unit for subsequent conversion into a biofuel. By at least partially transforming the soluble carbohydrates into a reaction product before the hydrolysate reaches the catalytic reduction reactor unit, demands on the catalytic reduction reactor unit may be lessened, and it may be possible to realize a higher conversion of soluble carbohydrates into the reaction product. In addition, it may be possible to use a smaller catalytic reduction reactor unit than in related processes, since at least a portion of the soluble carbohydrates have already been transformed prior to reaching the catalytic reduction reactor unit. Still further, since better heat integration efficiency may be realized by conducting a catalytic reduction reaction in the hydrothermal digestion unit, there may be a reduced need to recirculate the reaction product from the catalytic reduction reactor unit to the hydrothermal digestion unit in order to maintain an energy efficient process. Thus, lower reaction product recycle ratios may be used, and a greater fraction of the reaction product may be withdrawn for subsequent conversion into a biofuel or other materials. The foregoing factors may also reduce capital and operational costs associated with the biomass conversion systems and associated methods.

[0026] In further regard to heat integration efficiency, the present biomass conversion systems may also be particularly advantageous, since the hydrothermal digestion unit in the systems can be continuously operated at elevated temperatures and pressures, in some embodiments. Continuous, high temperature hydrothermal digestion may be accomplished by configuring the biomass conversion systems such that fresh biomass may be continuously or semi-continuously supplied

to the hydrothermal digestion unit, while it operates in a pressurized state. Without the ability to introduce fresh biomass to a pressurized hydrothermal digestion unit, depressurization and cooling of the hydrothermal digestion unit may take place during biomass addition, significantly reducing the energy- and cost-efficiency of the conversion process. As used herein, the term “continuous addition” and grammatical equivalents thereof will refer to a process in which cellulosic biomass is added to a hydrothermal digestion unit in an uninterrupted manner without fully depressurizing the hydrothermal digestion unit. As used herein, the term “semi-continuous addition” and grammatical equivalents thereof will refer to a discontinuous, but as-needed, addition of biomass to a hydrothermal digestion unit without fully depressurizing the hydrothermal digestion unit. A further description of solids introduction mechanisms that may supply biomass to a pressurized hydrothermal digestion unit are described in more detail below.

[0027] In some embodiments described herein, a slurry catalyst may be used both in the hydrothermal digestion unit and in the catalytic reduction reactor unit to mediate the catalytic reduction reaction of soluble carbohydrates into a reaction product. Use of a slurry catalyst, particularly in the hydrothermal digestion unit, may be advantageous, since a fixed bed catalyst would be highly susceptible to plugging in the presence of cellulosic biomass solids. Further, by using a slurry catalyst in the catalytic reduction reactor unit, there is a reduced likelihood of plugging from solids such as cellulosic biomass fines, for example. Still further, by using a slurry catalyst in both the hydrothermal digestion unit and the catalytic reduction reactor unit, there is no requirement to sequester the catalyst in either location, and it may circulate freely between the two, in some embodiments. However, in some embodiments, catalyst sequestration in the hydrothermal digestion unit, the catalytic reduction reactor unit, or both may be performed. Due to the presence of the cellulosic biomass solids in the hydrothermal digestion unit, the slurry catalyst may advantageously be at least partially retained therein by the cellulosic biomass charge, thereby lessening the need to perform catalyst sequestration as in other slurry catalyst processes. Retention of the slurry catalyst in the hydrothermal digestion unit may also be aided by the low recycle ratios that may be used in the biomass conversion systems described herein. In any event, circulation of the slurry catalyst through the cellulosic biomass charge within the hydrothermal digestion unit can provide good catalyst distribution within the biomass, thereby allowing soluble carbohydrates to be effectively stabilized via a catalytic reduction reaction as soon as possible following their formation.

[0028] Since a slurry catalyst can be fluidly mobile, hydrogen sparge, solvent recycle, or any combination thereof may be used to distribute the slurry catalyst throughout the cellulosic biomass charge in the hydrothermal digestion unit. Good catalyst distribution in the cellulosic biomass may improve yields by intercepting soluble carbohydrates before they have an opportunity to degrade. Furthermore, use of a slurry catalyst may allow a fixed bed digestion unit to be more successfully used, since mechanical stirring or like mechanical agitation is not needed to affect catalyst distribution. This can allow higher biomass to solvent ratios to be utilized per unit volume of the digestion unit than would be possible in stirred tank or like digestion unit configurations. Further-

more, since stirring is not necessary, there is no express need to alter the size of the biomass solids prior to digestion taking place.

[0029] Unless otherwise specified herein, it is to be understood that use of the terms “biomass” or “cellulosic biomass” in the description herein refers to “cellulosic biomass solids.” Solids may be in any size, shape, or form. The cellulosic biomass solids may be natively present in any of these solid sizes, shapes, or forms, or they may be further processed prior to hydrothermal digestion. In some embodiments, the cellulosic biomass solids may be chopped, ground, shredded, pulverized, and the like to produce a desired size prior to hydrothermal digestion. In some or other embodiments, the cellulosic biomass solids may be washed (e.g., with water, an acid, a base, combinations thereof, and the like) prior to hydrothermal digestion taking place.

[0030] In practicing the present embodiments, any type of suitable biomass source may be used. Suitable cellulosic biomass sources may include, for example, forestry residues, agricultural residues, herbaceous material, municipal solid wastes, waste and recycled paper, pulp and paper mill residues, and any combination thereof. Thus, in some embodiments, a suitable cellulosic biomass may include, 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 any combination thereof. Leaves, roots, seeds, stalks, husks, and the like may be used as a source of the cellulosic biomass. Common sources of cellulosic biomass may include, for example, agricultural wastes (e.g., corn stalks, straw, seed hulls, sugarcane leavings, nut shells, and the like), wood materials (e.g., wood or bark, sawdust, timber slash, mill scrap, and the like), municipal waste (e.g., waste paper, yard clippings or debris, and the like), and energy crops (e.g., poplars, willows, switch grass, alfalfa, prairie bluestem, corn, soybeans, and the like). The cellulosic biomass may be chosen based upon considerations such as, for example, cellulose and/or hemicellulose content, lignin content, growing time/season, growing location/transportation cost, growing costs, harvesting costs, and the like.

[0031] Illustrative carbohydrates that may be present in cellulosic biomass may include, for example, sugars, sugar alcohols, celluloses, lignocelluloses, hemicelluloses, and any combination thereof. Once soluble carbohydrates have been removed from the biomass matrix through a digestion process according to the embodiments described herein, the soluble carbohydrates may be transformed into a reaction product comprising oxygenated intermediates via a catalytic reduction reaction. In some embodiments, the oxygenated intermediates comprising the reaction product may be further transformed into a biofuel or other materials using any combination of further hydrogenolysis reactions, hydrogenation reactions, condensation reactions, isomerization reactions, oligomerization reactions, hydrotreating reactions, alkylation reactions, and the like. In some embodiments, at least a portion of the oxygenated intermediates may be recirculated to the hydrothermal digestion unit to comprise at least a portion of the digestion solvent. Recirculation of at least a portion of the oxygenated intermediates to the hydrothermal digestion unit may also be particularly advantageous in terms of heat integration and process efficiency.

[0032] In some embodiments, biomass conversion systems described herein can comprise: a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular

hydrogen (“molecular hydrogen activating slurry catalyst”); an optional hydrogen feed line that is operatively connected to the hydrothermal digestion unit; and a fluid circulation loop comprising the hydrothermal digestion unit and a catalytic reduction reactor unit, the catalytic reduction reactor unit also containing the slurry catalyst.

[0033] In some embodiments, cellulosic biomass solids may be introduced continuously to the hydrothermal digestion unit. In other embodiments, cellulosic biomass solids may be introduced non-continuously to the hydrothermal digestion unit. In various embodiments, the hydrothermal digestion unit may be operated continuously in a pressurized state (e.g., at a pressure of at least about 30 bar) to produce a hydrolysate comprising soluble carbohydrates, which are converted in situ in a catalytic reduction reaction into a more stable reaction product. Maintaining the pressurized state can promote the digestion of cellulosic biomass solids at a desirably rapid rate. In some embodiments, cellulosic biomass solids may be continuously added to the hydrothermal digestion unit while maintaining a pressurized state. In some embodiments, cellulosic biomass solids may be added semi-continuously to the hydrothermal digestion unit while maintaining a pressurized state.

[0034] In various embodiments, the fluid circulation loop may be configured to establish upward fluid flow in the catalytic reduction reactor unit. That is, in the biomass conversion systems described herein, the catalytic reduction reactor unit may be operated as a bubble column catalytic reduction reactor in such embodiments. In some embodiments, there may be a slurry catalyst sequestration mechanism that is operable to maintain at least a portion of the slurry catalyst within the catalytic reduction reactor unit. For example, in some embodiments, a catalyst screen or filter can be used in conjunction with the catalytic reduction reactor unit. Such catalyst screens and filters will be familiar to one having ordinary skill in the art. Catalyst filters or screens may include wire mesh or sintered metal or ceramic filters. Beds of solids such as, for example, sharp sands or other packed beds of solids, typically with a void fraction of about 25% or less by volume, may also be deployed as catalytic filters to separate slurry catalyst from a liquid filtrate. External filters such as cake filters, for example, may be deployed, where the filter media can be cloth, sintered metal, metal screens or fabrics, porous ceramic, pressed felts or cotton batting, nonwoven fabrics, filter paper, polymer membranes, or granular beds of particulate solids. Filters using these filter media may include cake filters, horizontal or vertical plate filters, filter presses, leaf filters, tubular filters, rotary drum filters, centrifugal discharge filters, and the like. Centrifuges, hydroclones, and gravity settlers can also be used to separate slurry catalyst from a liquid phase and recycle slurry catalyst. A pump, screw, or belt, for example, may be used to transport the separated or enriched slurry catalyst back into the catalytic reduction reactor unit. In other embodiments, the catalytic reduction reactor unit may lack an internal catalyst sequestration mechanism, and the slurry catalyst may be simply circulated back to the hydrothermal digestion unit when the biomass conversion systems are operated.

[0035] In some embodiments, the hydrothermal digestion unit may be, for example, a pressure vessel of carbon steel, stainless steel, or a similar alloy. In some embodiments, a single hydrothermal digestion unit may be present. In other embodiments, two or more hydrothermal digestion units operating in parallel may be used. Suitable hydrothermal

digestion units may include, for example, the “PANDIATM Digester” (Voest-Alpine Industrienlagenbau GmbH, Linz, Austria), the “DEFIBRATOR Digester” (Sunds Defibrator AB Corporation, Stockholm, Sweden), the M&D (Messing & Durkee) digester (Bauer Brothers Company, Springfield, Ohio, USA) and the KAMYR Digester (Andritz Inc., Glens Falls, N.Y., USA). Suitable configurations for the hydrothermal digestion unit may include, for example, trickle bed, pile-type, fluidized bed, and stirred contact. Furthermore, co-current flow or countercurrent flow may be present in the digestion unit.

[0036] In some embodiments, the biomass conversion systems may further comprise a solids introduction mechanism that is operatively connected to the hydrothermal digestion unit. The solids introduction mechanism may facilitate the introduction of cellulosic biomass solids to the digestion unit and allow the digestion unit to maintain a pressurized state while further cellulosic biomass solids are being added. In various embodiments, the solids introduction mechanism may comprise a pressure transition zone that cycles between a lower pressure state and a higher pressure state. In some further embodiments, the solids introduction mechanism may further comprise an atmospheric pressure zone. In some embodiments, the solids introduction mechanism may comprise an atmospheric pressure zone and a pressure transition zone that cycles between atmospheric pressure and a higher pressure state. The choice of whether to include an atmospheric pressure zone will be determined by the location in which the solids introduction mechanism is used, as will be discussed in more detail hereinafter. In some embodiments, the solids introduction mechanism may be used to bring cellulosic biomass solids from a low pressure state to a high pressure state suitable for being introduced to the pressurized hydrothermal digestion unit. In some embodiments, the solids introduction mechanism may be used to bring cellulosic biomass solids from atmospheric pressure to a high pressure state suitable for being introduced to the hydrothermal digestion unit.

[0037] When present, suitable atmospheric pressure zones may include, for example, conveyer belts, vibrational tube conveyers, screw feeders or conveyers, holding tanks, surge vessels, bin dispensers, and the like. Suitable pressure transition zones that are operable for continuous or semi-continuous addition of cellulosic biomass solids to a pressurized digestion unit may include, for example, pressurized screw feeders, pressure-cycling chambers, and the like as described in commonly owned United States Patent Application Publications 2013/0152457 and 2013/0152458, incorporated herein by reference in its entirety. In some embodiments, even when raising the pressure of cellulosic biomass solids from atmospheric pressure to an elevated pressure, the atmospheric pressure zone may be optionally omitted. That is, in such embodiments, the cellulosic biomass solids may be directly added to the pressure transition zone and pressure cycled for introduction to the pressurized digestion unit.

[0038] In some embodiments, the solids introduction mechanism may allow cellulosic biomass solids to be introduced to the hydrothermal digestion unit without the digestion unit being fully depressurized. Pressurizing the cellulosic biomass solids prior to introduction to the digestion unit may allow the digestion unit to remain pressurized and operating continuously. This can help maintain heat integration and energy efficiency of the biomass digestion process, as

noted above. Additional benefits of pressurizing the cellulosic biomass solids prior to digestion are also discussed hereinafter.

[0039] In some embodiments, pressurization of the pressure transition zone of the solids introduction mechanism may take place, at least in part, by introducing at least a portion of the liquor phase in the digestion unit to the pressure transition zone. In some or other embodiments, pressurization of the pressure transition zone may take place, at least in part, by introducing a gas to the pressure transition zone. In some embodiments, the liquor phase may comprise an organic solvent, which is generated as a reaction product of a catalytic reduction reaction. In other embodiments, an external solvent may be used to pressurize the pressure transition zone.

[0040] At least two benefits may be realized by pressurizing the cellulosic biomass solids using a liquor phase from the digestion unit. First, pressurizing the biomass solids in the presence of the liquor phase may cause the digestion solvent to infiltrate the biomass, which may cause the biomass to sink in the digestion solvent once introduction to the digestion unit takes place. Further, by adding hot liquor phase to the biomass solids in the pressure transition zone, less energy may need to be input to bring the biomass up to temperature once it is introduced to the digestion unit. Both of these features may improve the efficiency of the digestion process.

[0041] In some embodiments, the slurry catalyst may comprise a poison-tolerant catalyst. Use of a poison-tolerant catalyst may be particularly desirable, since catalyst poisons are not removed from the cellulosic biomass solids before hydrothermal digestion and integrated catalytic reduction take place. As used herein, a “poison-tolerant catalyst” is defined as 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 avoid the disadvantages of process downtime that are associated with catalyst regeneration and replacement. In addition to lost production time, considerable energy expenditure may be needed when restarting the hydrothermal digestion process.

[0042] In some embodiments, suitable poison-tolerant catalysts may include, for example, a sulfided catalyst. Sulfided catalysts suitable for activating molecular hydrogen are described in commonly owned United States Patent Application Publications 2012/0317872, 2012/0317873 and 2013/0109896, each of which is incorporated herein by reference in its entirety. Sulfiding may take place by treating a catalyst with hydrogen sulfide, optionally while the catalyst is deposited on a solid support. In more particular embodiments, the poison-tolerant catalyst may comprise a sulfided cobalt-molybdate catalyst. We have found that sulfided cobalt-molybdate catalysts, depending on the reaction conditions, may produce C2-C6 monohydric alcohols, diols (including glycols), triols, and combinations thereof, while not forming an excessive amount of C2-C4 alkanes. As used herein, the term “monohydric alcohol” refers to an organic molecule containing a single alcohol functional group. Monohydric alcohols formed may be readily separated from water via flash vaporization or liquid-liquid phase separation, and undergo condensation-oligomerization reactions in separate steps over an acid or base catalyst, to produce liquid biofuels in the gasoline, jet, or diesel range. Slurry catalysts containing Pt or Pd may be particularly useful poison-tolerant catalysts for use in the present embodiments.

[0043] 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 then added to the hydrothermal digestion unit.

[0044] In some embodiments, the slurry catalyst may be regenerable. For example, in some embodiments, the slurry catalyst may be regenerable through exposure to water at a temperature above its normal boiling point. As used herein, a “regenerable catalyst” may have at least some of its catalytic activity restored through regeneration, even when poisoned with nitrogen compound impurities, sulfur compound impurities, or any combination thereof. Ideally, such regenerable catalysts should be regenerable with a minimal amount of process downtime. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least about 200° C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least about 250° C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least about 300° C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least about 350° C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least about 400° C. The water used for regenerating the slurry catalyst may be in a subcritical state or a supercritical state. A particularly suitable slurry catalyst that can be regenerated through exposure to water above its normal boiling point is ruthenium disposed on a solid support such as, for example, ruthenium on titanium dioxide or ruthenium on carbon. Other suitable slurry catalysts may include a platinum or palladium compound disposed on a solid support. Most catalysts effective for mediating a catalytic reduction reaction are also regenerable, at least in part, through thermal treatments with hydrogen. Regeneration of the slurry catalyst may take place in the hydrothermal digestion unit, the catalytic reduction reactor unit, or elsewhere, if desired.

[0045] In some embodiments, the slurry catalyst 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 platinum, palladium, ruthenium, nickel, cobalt, or other Group VIII metals alloyed or modified with rhenium, molybdenum, tin, or other metals. Thus, in some embodiments described herein, an external hydrogen feed may not be needed. However, in other embodiments, an external hydrogen feed may be used, optionally in combination with internally generated hydrogen.

[0046] In various embodiments, the slurry catalyst 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. In some embodiments, the slurry catalyst may have a particulate size of 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. As used herein, the term “catalyst fines” refers to solid catalysts having a nominal particulate

size of about 100 microns or less. Catalyst fines may be generated from catalyst production processes, for example, during extrusion of solid catalyst. Catalyst fines may also be produced by grinding larger catalyst solids or during regeneration of catalyst solids. Suitable methods for producing catalyst fines are described in U.S. Pat. Nos. 6,030,915 and 6,127,299, each of which is incorporated herein by reference in its entirety. In some instances, catalyst fines may be removed from a solid catalyst production run, since they may be difficult to sequester in some catalytic processes. Techniques for removing catalyst fines from larger catalyst solids may include, for example, sieving or like size separation processes. Since there is no requirement to retain the catalyst in a fixed location in the embodiments described herein, catalyst fines may be particularly well tolerated. Advantageously, due to their small size, catalyst fines may be easily fluidized and distributed throughout the cellulosic biomass solids.

[0047] In some embodiments, the catalytic reduction reactions carried out in the hydrothermal digestion unit and the catalytic reduction reactor unit may be hydrogenolysis reactions. A detailed description of hydrogenolysis reactions is included hereinbelow.

[0048] In some embodiments, the fluid circulation loop may be configured to establish upward fluid flow in the hydrothermal digestion unit. As used herein, the term “upward fluid flow,” also referred to herein as “countercurrent flow,” refers to the direction a reaction product enters the hydrothermal digestion unit relative to the direction in which biomass is introduced to the digestion unit. By upwardly flowing a fluid containing a slurry catalyst into a cellulosic biomass charge, the slurry catalyst may become well distributed throughout. Specifically, upward fluid flow may work against gravity-induced compaction of the cellulosic biomass charge, thereby making distribution of the slurry catalyst more facile. Other flow configurations such as, for example, co-current flow may also be used, if desired.

[0049] In some embodiments, the hydrothermal digestion units of the biomass conversion systems described herein may contain a retention mechanism for maintaining cellulosic biomass therein. In some embodiments, the retention mechanism within the hydrothermal digestion unit may be operable to retain cellulosic biomass solids that have a particle size of about 3 mm or above. That is, when a retention mechanism is present, cellulosic biomass fines and slurry catalyst may be free to circulate throughout the biomass conversion systems, but the larger cellulosic biomass particles may be retained within the hydrothermal digestion unit. Suitable retention mechanisms may include, for example, screens and the like.

[0050] In some embodiments, there may be a reaction product takeoff line in fluid communication with the fluid circulation loop, where the reaction product takeoff line is located between the hydrothermal digestion unit and an outlet of the catalytic reduction reactor unit. In some embodiments, there may be a solids separation mechanism that is operatively connected to the reaction product takeoff line. A solids separation mechanism in this location may be used to remove solids from the reaction product before it is further transformed downstream into a biofuel or other substance. In some embodiments, a reaction product takeoff line may be operatively connected to the hydrothermal digestion unit. The reaction product takeoff line operatively connected to the hydrothermal digestion unit may be present instead of, or in

addition to, the reaction product takeoff line between the hydrothermal digestion unit and an outlet of the catalytic reduction reactor unit.

[0051] Solids separation mechanisms suitable for inclusion in the reaction product takeoff line or elsewhere in the biomass conversion systems may involve any separation technique known in the art including, for example, filters, centrifugal force- or centrifugal force-based separation mechanisms (e.g., hydroclones), settling tanks, centrifuges, and the like. Suitable filters may include, for example, surface filters and depth filters. Surface filters may include, for example, filter papers, membranes, porous solid media, and the like. Depth filters may include, for example, a column or plug of porous media designed to trap solids within its core structure. In some embodiments, two or more filters may be used, where at least one of the filters may be backflushed while forward fluid flow continues through at least some of the remaining filters. In some embodiments, one or more hydroclones may be used.

[0052] Although a solids separation may also be performed in the fluid circulation loop, if desired, a solids separation is typically not needed in this location, since both the hydrothermal digestion unit and the catalytic reduction reactor unit may contain particulate matter (e.g., the slurry catalyst).

[0053] The biomass conversion systems of the foregoing description will now be further described with reference to the drawing. FIG. 1 shows a schematic of an illustrative biomass conversion system having a hydrothermal digestion unit and a catalytic reduction reactor unit coupled to one another in a fluid circulation loop, where both the hydrothermal digestion unit and the catalytic reduction reactor unit contain a slurry catalyst. Biomass conversion system 1 contains hydrothermal digestion unit 2, which is in fluid communication with catalytic reduction reactor unit 4 via fluid circulation loop 10. As drawn, fluid circulation loop 10 is configured to establish upward fluid flow in hydrothermal digestion unit 2. Other types of fluid connections to hydrothermal digestion unit 2 are also possible. The direction of biomass introduction into hydrothermal digestion unit 2 and flow of bulk biomass therein is indicated by a dashed arrow. Optional hydrogen feed line 8 is operatively connected to hydrothermal digestion unit 2. An optional hydrogen feed line may also be operatively connected to catalytic reduction reactor unit 4 but has not been depicted for purposes of clarity. Catalyst particles 9 and 9' may be present in hydrothermal digestion unit 2 and catalytic reduction reactor unit 4, respectively. As depicted in FIG. 1, fluid circulation loop 10 is configured such that a fluid flows through catalytic reduction reactor unit 4 in an upward manner.

[0054] Cellulosic biomass solids may be introduced to hydrothermal digestion unit 2 by solids introduction mechanism 14, which comprises atmospheric pressure zone 15 and pressure transition zone 16. Atmospheric pressure zone 15 may include structures such as hoppers, bins, and the like that are capable of holding cellulosic biomass solids for introduction to hydrothermal digestion unit 2. Pressure transition zone 16 may comprise any structure that is capable of increasing the pressure of solids being introduced to hydrothermal digestion unit 2. Pressure transition zone 16 is also capable of cycling between atmospheric pressure and an elevated pressure state. Optionally, solids introduction mechanism 14 may be omitted, and cellulosic biomass solids may be directly added to pressure transition zone 16 for introduction into hydrothermal digestion unit 2.

[0055] Biomass conversion system **1** also contains reaction product takeoff line **18**, which is in fluid communication with fluid circulation loop **10** after the outlet of catalytic reduction reactor unit **4**. During operation of biomass conversion system **1**, a reaction product may exit catalytic reduction reactor unit **4** and flow through line **20**. At this point, the reaction product may then be removed from fluid circulation loop **10** by reaction product takeoff line **18** or recirculate to hydrothermal digestion unit **2** by line **22**. Reaction product removed by reaction product takeoff line **18** may then undergo subsequent further transformation into a biofuel. Reaction product in reaction product takeoff line **18** may have solids removed therefrom by optional solids separation mechanism **24**. Suitable solids separation mechanisms may include, for example, one or more filters, one or more hydroclones, centrifuges, membranes, settling tanks, and the like, as discussed in further detail above. Reaction product returned to hydrothermal digestion unit **2** via line **22** may serve as a digestion solvent or undergo further conversion into the reaction product, for example.

[0056] Various additional optional elements may be present in biomass conversion system **1**. One optional element that may be included in biomass conversion system **1** is phase separation mechanism **26**, which is in fluid communication with line **20**. As described in further detail below, phase separation mechanism **26** may be used to at least partially separate the organic phase of the reaction product from an aqueous phase. Other locations for phase separation mechanism **26** are possible.

[0057] Optional line **30** may be used to transfer liquor phase from hydrothermal digestion unit **2**. As depicted in FIG. **1**, line **30** may be used to transfer liquor phase from hydrothermal digestion unit **2** to at least partially pressurize pressure transition zone **16** of solids introduction mechanism **14**. Other configurations for line **30** are possible. Cellulosic biomass solids may be supplied to pressure transition zone **16** from atmospheric pressure zone **15** before pressurizing and introducing the pressurized biomass to hydrothermal digestion unit **2**. Through use of pressure transition zone **16**, hydrothermal digestion unit **2** does not have to be fully depressurized during the addition of cellulosic biomass solids, thereby allowing the digestion process to proceed in a substantially uninterrupted manner.

[0058] In some embodiments, methods for processing cellulosic biomass solids can comprise: providing cellulosic biomass solids in a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular hydrogen; heating the cellulosic biomass solids in the hydrothermal digestion unit in the presence of molecular hydrogen while circulating the slurry catalyst therethrough, thereby forming a hydrolysate comprising soluble carbohydrates within a liquor phase; at least partially transforming the soluble carbohydrates into a reaction product while the soluble carbohydrates are within the hydrothermal digestion unit; and transferring at least a portion of the liquor phase to a catalytic reduction reactor unit that also contains the slurry catalyst, so as to further transform the soluble carbohydrates into the reaction product.

[0059] In some embodiments, methods for processing cellulosic biomass solids can comprise: providing a biomass conversion system that comprises: a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular hydrogen, an optional hydrogen feed line that is operatively connected to the hydrothermal digestion unit, and

a fluid circulation loop comprising the hydrothermal digestion unit and a catalytic reduction reactor unit that also contains the slurry catalyst; heating cellulosic biomass solids in the hydrothermal digestion unit in the presence of molecular hydrogen while circulating the slurry catalyst therethrough, thereby forming a hydrolysate comprising soluble carbohydrates within a liquor phase; at least partially transforming the soluble carbohydrates into a reaction product while the soluble carbohydrates are within the hydrothermal digestion unit; and transferring at least a portion of the liquor phase to the catalytic reduction reactor unit, so as to further transform the soluble carbohydrates into the reaction product.

[0060] In some embodiments, prior to digestion, the cellulosic biomass may be washed and/or reduced in size (e.g., by chopping, crushing, debarking, and the like) to achieve a desired size and quality for being digested. The operations may remove substances that interfere with further chemical transformation of soluble carbohydrates and/or improve the penetration of digestion solvent into the biomass. In some embodiments, washing may occur within the hydrothermal digestion unit prior to pressurization. In other embodiments, washing may occur before the biomass is placed in the hydrothermal digestion unit.

[0061] In general, digestion in the hydrothermal digestion unit may be conducted in a liquor phase. In some embodiments, the liquor phase may comprise a digestion solvent that comprises water. In some embodiments, the liquor phase may further comprise an organic solvent. In some embodiments, the organic solvent may comprise oxygenated intermediates produced from a catalytic reduction reaction of soluble carbohydrates. For example, in some embodiments, a digestion solvent may comprise oxygenated intermediates produced by a hydrogenolysis reaction or other catalytic reduction reaction of soluble carbohydrates. In some embodiments, the oxygenated intermediates may include those produced from an in situ catalytic reduction reaction and/or from the catalytic reduction reactor unit. In some embodiments, bio-ethanol may be added to water as a startup digestion solvent, with a solvent comprising oxygenated intermediates being produced thereafter. Any other organic solvent that is miscible with water may also be used as a startup digestion solvent, if desired. In general, a sufficient amount of liquor phase may be present in the digestion process such that the biomass surface remains wetted. The amount of liquor phase may be further chosen to maintain a sufficiently high concentration of soluble carbohydrates to attain a desirably high reaction rate during catalytic reduction, but not so high such that degradation becomes problematic. In some embodiments, the concentration of soluble carbohydrates may be kept below about 5% by weight of the liquor phase to minimize degradation. However, it is to be recognized that higher concentrations may be used in some embodiments. In some embodiments, organic acids such as, for example, acetic acid, oxalic acid, salicylic acid, or acetylsalicylic acid may be included in the liquor phase as an acid promoter of the digestion process.

[0062] In some embodiments, the digestion solvent may comprise an organic solvent comprising oxygenated intermediates resulting from a catalytic reduction reaction of soluble carbohydrates. The catalytic reduction reaction may take place within the hydrothermal digestion unit and/or in the catalytic reduction reactor unit. In some embodiments, the organic solvent may comprise at least one alcohol, ketone, or polyol. In alternative embodiments, the digestion solvent may be at least partially supplied from an external source. For

example, in some embodiments, bio-ethanol may be used to supplement the organic solvent. Other water-miscible organic solvents may be used as well. In some embodiments, the digestion solvent may be separated, stored, or selectively injected into the hydrothermal digestion unit so as to maintain a desired concentration of soluble carbohydrates or to provide temperature regulation in the hydrothermal digestion unit.

[0063] In various embodiments, digestion may take place over a period of time at elevated temperatures and pressures. In some embodiments, digestion may take place at a temperature ranging between about 100° C. to about 240° C. for a period of time. In some embodiments, the period of time may range between about 0.25 hours and about 24 hours. In some embodiments, the digestion to produce soluble carbohydrates may occur at a pressure ranging between about 1 bar (absolute) and about 100 bar. In general, the higher the temperature, the shorter the amount of time needed for hydrothermal digestion steps to take place. As an example, hydrothermal digestion may take place for about 1 hour to about 10 hours at a temperature of about 180° C. to about 270° C., most typically from about 190° C. to about 250° C.

[0064] In various embodiments, suitable biomass digestion techniques may include, for example, acid digestion, alkaline digestion, enzymatic digestion, and digestion using hot-compressed water.

[0065] In some embodiments, the methods may further comprise withdrawing at least a portion of the reaction product from the biomass conversion system (e.g., from the outlet of the catalytic reduction reactor unit or from the fluid circulation loop). In some embodiments, the methods may further comprise converting the reaction product into a biofuel, as described in further detail hereinafter. In some embodiments, the methods may further comprise separating solids (e.g., slurry catalyst, biomass fines, and the like) from the reaction product after its withdrawal from the biomass conversion system, as described above.

[0066] In some embodiments, the methods may further comprise recirculating at least a portion of the liquor phase from the catalytic reduction reactor unit to the hydrothermal digestion unit. As set forth above, the biomass conversion systems described herein are particularly advantageous in being capable of rapidly at least partially transforming soluble carbohydrates into a reaction product comprising oxygenated intermediates by performing an in situ catalytic reduction reaction in the hydrothermal digestion unit. As also noted above, the liquor phase containing the reaction product may be recirculated from the catalytic reduction reactor unit to the hydrothermal digestion unit, where the liquor phase may, for example, help regulate temperature therein, serve as a digestion solvent, and the like. Recirculation from the catalytic reduction reactor unit to the hydrothermal digestion unit may take place at various recycle ratios. As used herein, the term “recycle ratio” refers to the amount of liquor phase that is recirculated to the hydrothermal digestion unit (e.g., within the fluid circulation loop) relative to the amount of liquor phase that is withdrawn from the biomass conversion system (e.g., by a reaction product takeoff line).

[0067] A particular benefit of performing an in situ catalytic reduction reaction in the hydrothermal digestion unit is that lower recycle ratios may be used when recirculating the liquor phase to the hydrothermal digestion, while still maintaining process efficiency and yields. Specifically, there may be less need to supply heat from the recirculated reaction product to the digestion process occurring in the hydrother-

mal digestion unit, given that an exothermic catalytic reduction reaction is already taking place therein. Accordingly, a relatively high proportion of the liquor phase exiting the catalytic reduction reactor unit may be withdrawn from the biomass conversion system for subsequent conversion into a biofuel. Lower recycle ratios may also allow smaller reactor volumes to be used, as total liquid flow velocity in the hydrothermal digestion unit and catalytic reduction reactor are reduced. High recycle ratios and high liquid flow velocities may give rise to excessive pressure drops, high pump energy and size requirements, and other adverse features. Failure to minimize residence time prior to stabilization via a catalytic reduction reaction may also result in lower yields. Given the benefit of the present disclosure, one having ordinary skill in the art will be able to determine an appropriate recycle ratio for liquor phase recirculation that achieves a desired amount of heat integration, while balancing a desired rate of downstream biofuel production. In some embodiments, the liquor phase may be recirculated from the catalytic reduction reactor unit to the hydrothermal digestion unit at a recycle ratio ranging between about 0.2 and about 10. In some embodiments, the liquor phase may be recirculated from the catalytic reduction reactor unit to the hydrothermal digestion unit at a recycle ratio ranging between about 1 and about 10, or between about 1 and about 5, or between about 0.2 and about 2, or between about 0.5 and about 2, or between about 1 and about 2, or between about 0.2 and about 1, or between about 0.5 and about 1. In some embodiments, the liquor phase may be recirculated from the catalytic reduction reactor unit to the hydrothermal digestion unit at a recycle ratio of about 2 or less. In some embodiments, the liquor phase may be recirculated from the catalytic reduction reactor unit to the hydrothermal digestion unit at a recycle ratio of about 1 or less. In some embodiments, the liquor phase may be recirculated from the catalytic reduction reactor unit to the hydrothermal digestion unit such that upward fluid flow is established in the hydrothermal digestion unit. In other embodiments, other flow patterns may be established in the hydrothermal digestion unit, including co-current flow, for example.

[0068] In some embodiments, heating the cellulosic biomass solids in the hydrothermal digestion unit may take place at a pressure of at least about 30 bar. Maintaining digestion at a pressure of at least about 30 bar may ensure that digestion takes place at a satisfactory rate. In some embodiments, heating the cellulosic biomass solids in the hydrothermal digestion unit may take place at a pressure of at least about 60 bar. In some embodiments, heating the cellulosic biomass solids in the hydrothermal digestion unit may take place at a pressure of at least about 90 bar. In some embodiments, heating the cellulosic biomass solids in the hydrothermal digestion unit may take place at a pressure ranging between about 30 bar and about 430 bar. In some embodiments, heating the cellulosic biomass solids in the hydrothermal digestion unit may take place at a pressure ranging between about 50 bar and about 330 bar. In some embodiments, heating the cellulosic biomass solids in the hydrothermal digestion unit may take place at a pressure ranging between about 70 bar and about 130 bar. In some embodiments, heating the cellulosic biomass solids in the hydrothermal digestion unit may take place at a pressure ranging between about 30 bar and about 130 bar. It is to be noted that the foregoing pressures refer to the pressures at which digestion takes place. That is, the foregoing pressures refer to normal operating pressures for the hydrothermal digestion unit.

[0069] Since the present biomass conversion systems provide stabilization of soluble carbohydrates by performing an in situ catalytic reduction reaction in the hydrothermal digestion unit, longer contact times are more feasible, since degradation of the soluble carbohydrates is less of a concern. In some embodiments, the contact time period may be about 1 hour or more. In some embodiments, the contact time period may be about 2 hours or more, or about 4 hours or more, or about 6 hours or more, or about 8 hours or more, or about 10 hours or more, or about 12 hours or more, or about 24 hours or more. For batch processing, in particular, times ranging from about 1 hour to about 24 hours may be used.

[0070] In general, after digestion in the hydrothermal digestion unit takes place, only small percentages of the original cellulosic biomass solids may remain undigested. In some embodiments, after heating in the hydrothermal digestion unit (e.g., at the second temperature and for the second time period), less than about 40% of the cellulosic biomass solids, on a dry basis may remain undigested. In some embodiments, after heating in the hydrothermal digestion unit less than about 30% of the cellulosic biomass solids, on a dry basis may remain undigested. In some embodiments, after heating in the hydrothermal digestion unit less than about 20% of the cellulosic biomass solids, on a dry basis may remain undigested. In some embodiments, after heating in the hydrothermal digestion unit less than about 10% of the cellulosic biomass solids, on a dry basis may remain undigested.

[0071] In some embodiments, a poison-tolerant slurry catalyst may be used in the methods. Suitable poison-tolerant slurry catalysts have been set forth above. In some embodiments, a regenerable catalyst may be used in the methods. In some embodiments, the methods may further comprise regenerating the slurry catalyst. In some embodiments, the methods may further comprise regenerating the slurry catalyst through exposure to water having a temperature of at least about 200° C., or at least about 250° C., or at least about 300° C., or at least about 350° C., or at least about 400° C.

[0072] In some embodiments, the present methods may further comprise performing a phase separation of the reaction product. In some embodiments, phase separation may take place using a phase separation mechanism that is present following an outlet of the catalytic reduction reactor unit. In various embodiments, performing a phase separation may comprise separating a bilayer, conducting a solvent stripping operation, performing an extraction, performing a filtration, performing a distillation, or the like. In some embodiments, azeotropic distillation may be conducted.

[0073] In some embodiments, the methods described herein may further comprise converting the reaction product into a biofuel. In some embodiments, conversion of the reaction product into a biofuel may begin with a catalytic hydrogenolysis reaction to transform soluble carbohydrates produced from hydrothermal digestion into a reaction product comprising oxygenated intermediates, as described above. As further described above, a liquor phase containing the reaction product may be recirculated to the hydrothermal digestion unit to further aid in the digestion process. In some embodiments, the reaction product may be further transformed by any number of further catalytic reforming reactions including, for example, further catalytic reduction reactions (e.g., hydrogenolysis reactions, hydrogenation reactions, hydrotreating reactions, and the like), condensation reactions, isomerization reactions, desulfurization reactions, dehydration reactions, oligomerization reactions, alky-

lation reactions, and the like. A description of the initial hydrogenolysis reaction and the further catalytic reforming reactions are described hereinafter.

[0074] Various processes are known for performing hydrogenolysis of carbohydrates. One suitable method includes contacting a carbohydrate or stable hydroxyl intermediate with hydrogen, optionally mixed with a diluent gas, and a hydrogenolysis catalyst under conditions effective to form a reaction product comprising oxygenated intermediates such as, for example, smaller molecules or polyols. As used herein, the term “smaller molecules or polyols” includes any molecule that have a lower molecular weight, which may include a smaller number of carbon atoms or oxygen atoms, than the starting carbohydrate. In some embodiments, the reaction products may include smaller molecules such as, for example, polyols and alcohols. This aspect of hydrogenolysis entails the breaking of carbon-carbon bonds

[0075] In some embodiments, a soluble carbohydrate may be converted to relatively stable oxygenated intermediates such as, for example, propylene glycol, ethylene glycol, and glycerol using a hydrogenolysis reaction in the presence of a catalyst that is capable of activating molecular hydrogen. Suitable catalysts may include, 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, such as the hydrogenation of a carbonyl group to form an alcohol. The catalyst may also include a carbonaceous pyropolymer catalyst containing transition metals (e.g., chromium, molybdenum, tungsten, rhenium, manganese, copper, and cadmium) or Group VIII metals (e.g., iron, cobalt, nickel, platinum, palladium, rhodium, ruthenium, iridium, and osmium). In certain embodiments, the catalyst may include any of the above metals combined with an alkaline earth metal oxide or adhered to a catalytically active support. In certain embodiments, the catalyst described in the hydrogenolysis reaction may include a catalyst support.

[0076] The conditions under 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), for example. 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 may be conducted at temperatures in the range of about 110° C. to about 300° C., and preferably from about 170° C. to about 300° C., and most preferably from about 180° C. to about 290° C.

[0077] In some embodiments, the hydrogenolysis reaction may be conducted under basic conditions, preferably at a pH of about 8 to about 13, and even more preferably at a pH of about 10 to about 12. In some embodiments, the hydrogenolysis reaction may be conducted at a pressure ranging between about 1 bar (absolute) and about 150 bar, and preferably at a pressure ranging between about 15 bar and about 140 bar, and even more preferably at a pressure ranging between 50 bar and 110 bar.

[0078] The hydrogen used in the hydrogenolysis reaction may include external hydrogen, recycled hydrogen, in situ generated hydrogen, or any combination thereof.

[0079] In some embodiments, the reaction products of the hydrogenolysis reaction may comprise greater than about

25% by mole, or alternatively, greater than about 30% by mole of polyols, which may result in a greater conversion to a biofuel in a subsequent processing reaction.

[0080] In some embodiments, hydrogenolysis may be conducted under neutral or acidic conditions, as needed to accelerate hydrolysis reactions in addition to the hydrogenolysis reaction. For example, hydrolysis of oligomeric carbohydrates may be combined with hydrogenation to produce sugar alcohols, which may undergo hydrogenolysis.

[0081] A second aspect of hydrogenolysis entails the breaking of —OH bonds such as: $\text{RC(H)}_2\text{—OH} + \text{H}_2 \rightarrow \text{RCH}_3 + \text{H}_2\text{O}$. 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 with increased temperature or contact time with catalyst, the concentration of polyols and diols relative to mono-oxygenates may diminish as a result of hydrodeoxygenation. Selectivity for C—C vs. C—OH bond hydrogenolysis will vary with catalyst type and formulation. Full de-oxygenation to alkanes may also occur, but is generally undesirable if the intent is to produce mono-oxygenates or diols and polyols which may be condensed or oligomerized to higher molecular weight compounds in a subsequent processing step. Typically, it is desirable to send only mono-oxygenates or diols to subsequent processing steps, as higher polyols may lead to excessive coke formation during condensation or oligomerization. Alkanes, in contrast, are essentially unreactive and cannot be readily combined to produce higher molecular compounds.

[0082] Once oxygenated intermediates have been formed by a hydrogenolysis reaction, a portion of the reaction product may be recirculated to the hydrothermal digestion unit to serve as an internally generated digestion solvent. Another portion of the reaction product may be withdrawn and subsequently processed by further reforming reactions to form a biofuel. Before being subjected to the further reforming reactions, the oxygenated intermediates may optionally be separated into different components. Suitable separations may include, for example, phase separation, solvent stripping columns, extractors, filters, distillations and the like. In some embodiments, a separation of lignin from the oxygenated intermediates may be conducted before the reaction product is subsequently processed further or recirculated to the hydrothermal digestion unit.

[0083] The oxygenated intermediates may be processed to produce a fuel blend in one or more processing reactions. In some embodiments, a condensation reaction may be used along with other reactions to generate a fuel blend and may be catalyzed by a catalyst comprising an acid, a base, or both. In general, without being limited to any particular theory, it is believed that the basic condensation reactions may involve 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 $>\text{C}_4$ 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. In some embodiments, a basic catalyst, a catalyst having both an acid and a base functional site, and optionally comprising a metal function, may also be used to effect the condensation reaction.

[0084] In some embodiments, an aldol condensation reaction may be used to produce a fuel blend meeting the requirements for a diesel fuel or jet fuel. Traditional diesel fuels are petroleum distillates rich in paraffinic hydrocarbons. They have boiling ranges as broad as 187°C . to 417°C ., which are suitable for combustion in a compression ignition engine, such as a diesel engine vehicle. The American Society of Testing and Materials (ASTM) establishes the grade of diesel according to the boiling range, along with allowable ranges of other fuel properties, such as cetane number, cloud point, flash point, viscosity, aniline point, sulfur content, water content, ash content, copper strip corrosion, and carbon residue. Thus, any fuel blend meeting ASTM D975 may be defined as diesel fuel.

[0085] The present disclosure also provides methods to produce jet fuel. Jet fuel is clear to straw colored. The most common fuel is an unleaded/paraffin oil-based fuel classified as Aeroplane A-1, which is produced to an internationally standardized set of specifications. Jet fuel is a mixture of a large number of different hydrocarbons, possibly as many as a thousand or more. The range of their sizes (molecular weights or carbon numbers) is restricted by the requirements for the product, for example, freezing point or smoke point. Kerosene-type Airplane fuel (including Jet A and Jet A-1) has a carbon number distribution between about C8 and C16. Wide-cut or naphtha-type Airplane fuel (including Jet B) typically has a carbon number distribution between about C5 and C15. A fuel blend meeting ASTM D1655 may be defined as jet fuel.

[0086] In certain embodiments, both Airplanes (Jet A and Jet B) contain a number of additives. Useful additives include, but are not limited to, antioxidants, antistatic agents, corrosion inhibitors, and fuel system icing inhibitor (FSII) agents. Antioxidants prevent gumming and usually, are based on alkylated phenols, for example, AO-30, AO-31, or AO-37. Antistatic agents dissipate static electricity and prevent sparking. Stadis 450 with dinonylnaphthylsulfonic acid (DINNSA) as the active ingredient, is an example. Corrosion inhibitors (e.g., DCI-4A) are used for civilian and military fuels, and DCI-6A is used for military fuels. FSII agents, include, for example, Di-EGME.

[0087] In some embodiments, the oxygenated intermediates may comprise a carbonyl-containing compound that may take part in a base catalyzed condensation reaction. In some embodiments, an optional dehydrogenation reaction may be used to increase the amount of carbonyl-containing compounds in the oxygenated intermediate stream to be used as a feed to the condensation reaction. In these embodiments, the oxygenated intermediates and/or a portion of the bio-based feedstock stream may be dehydrogenated in the presence of a catalyst.

[0088] In some embodiments, a dehydrogenation catalyst may be preferred for an oxygenated intermediate stream comprising alcohols, diols, and triols. In general, alcohols cannot participate in aldol condensation directly. The hydroxyl group or groups present may be converted into carbonyls (e.g., aldehydes, ketones, etc.) in order to participate in an aldol condensation reaction. A dehydrogenation catalyst may be included to effect dehydrogenation of any alcohols, diols,

or polyols present to form ketones and aldehydes. The dehydration catalyst is typically formed from the same metals as used for hydrogenation, hydrogenolysis, or aqueous phase reforming. These catalysts are described in more detail above. Dehydrogenation yields may be enhanced by the removal or consumption of hydrogen as it forms during the reaction. The dehydrogenation step may be carried out as a separate reaction step before an aldol condensation reaction, or the dehydrogenation reaction may be carried out in concert with the aldol condensation reaction. For concerted dehydrogenation and aldol condensation reactions, the dehydrogenation and aldol condensation functions may take place on the same catalyst. For example, a metal hydrogenation/dehydrogenation functionality may be present on catalyst comprising a basic functionality.

[0089] The dehydrogenation reaction may result in the production of a carbonyl-containing compound. Suitable carbonyl-containing compounds may include, but are not limited to, any compound comprising a carbonyl functional group that may form carbanion species or may react in a condensation reaction with a carbanion species. In an embodiment, a carbonyl-containing compound may include, but is not limited to, ketones, aldehydes, furfurals, hydroxy carboxylic acids, and, carboxylic acids. Ketones may include, without limitation, hydroxyketones, cyclic ketones, diketones, acetone, propanone, 2-oxopropanal, butanone, butane-2,3-dione, 3-hydroxybutane-2-one, pentanone, cyclopentanone, pentane-2,3-dione, pentane-2,4-dione, hexanone, cyclohexanone, 2-methyl-cyclopentanone, heptanone, octanone, nonanone, decanone, undecanone, dodecanone, methylglyoxal, butanedione, pentanedione, diketohexane, dihydroxyacetone, and isomers thereof. Aldehydes may include, without limitation, hydroxyaldehydes, acetaldehyde, glyceraldehyde, propionaldehyde, butyraldehyde, pentanal, hexanal, heptanal, octanal, nonal, decanal, undecanal, dodecanal, and isomers thereof. Carboxylic acids may include, without limitation, formic acid, acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, isomers and derivatives thereof, including hydroxylated derivatives, such as 2-hydroxybutanoic acid and lactic acid. Furfurals may include, without limitation, hydroxymethylfurfural, 5-hydroxymethyl-2(5H)-furanone, dihydro-5-(hydroxymethyl)-2(3H)-furanone, tetrahydro-2-furoic acid, dihydro-5-(hydroxymethyl)-2(3H)-furanone, tetrahydrofurfuryl alcohol, 1-(2-furyl)ethanol, hydroxymethyltetrahydrofurfural, and isomers thereof. In an embodiment, the dehydrogenation reaction may result in the production of a carbonyl-containing compound that is combined with the oxygenated intermediates to become a part of the oxygenated intermediates fed to the condensation reaction.

[0090] In an embodiment, an acid catalyst may be used to optionally dehydrate at least a portion of the oxygenated intermediate stream. Suitable acid catalysts for use in the dehydration reaction 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 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 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 solution.

[0091] In some embodiments, the dehydration reaction may occur in the vapor phase. In other embodiments, the dehydration reaction may occur in the liquid phase. For liquid phase dehydration reactions, an aqueous solution may be used to carry out the reaction. In an embodiment, other solvents in addition to water, may be used to form the aqueous solution. For example, water soluble organic solvents may be present. Suitable solvents may include, but are not limited to, hydroxymethylfurfural (HMF), dimethylsulfoxide (DMSO), 1-methyl-n-pyrrolidone (NMP), and any combination thereof. Other suitable aprotic solvents may also be used alone or in combination with any of these solvents.

[0092] In an embodiment, the processing reactions may comprise an optional ketonization reaction. A ketonization reaction may increase the number of ketone functional groups within at least a portion of the oxygenated intermediates. For example, an alcohol may be converted into a ketone in a ketonization reaction. Ketonization may be carried out in the presence of a basic catalyst. Any of the basic catalysts described above as the basic component of the aldol condensation reaction may be used to effect a ketonization reaction. Suitable reaction conditions are known to one of ordinary skill in the art and generally correspond to the reaction conditions listed above with respect to the aldol condensation reaction. The ketonization reaction may be carried out as a separate reaction step, or it may be carried out in concert with the aldol condensation reaction. The inclusion of a basic functional site on the aldol condensation catalyst may result in concerted ketonization and aldol condensation reactions.

[0093] In some embodiments, the processing reactions may comprise an optional furanic ring opening reaction. A furanic ring opening reaction may result in the conversion of at least a portion of any oxygenated intermediates comprising a furanic ring into compounds that are more reactive in an aldol condensation reaction. A furanic ring opening reaction may be carried out in the presence of an acidic catalyst. Any of the acid catalysts described above as the acid component of the aldol condensation reaction may be used to effect a furanic ring opening reaction. Suitable reaction conditions are known to one of ordinary skill in the art and generally correspond to the reaction conditions listed above with respect to the aldol condensation reaction. The furanic ring opening reaction may be carried out as a separate reaction step, or it may be carried out in concert with the aldol condensation reaction. The inclusion of an acid functional site on the aldol condensation catalyst may result in a concerted furanic ring opening reaction and aldol condensation reactions. Such an embodiment may be advantageous as any furanic rings may be opened in the presence of an acid functionality and reacted in an aldol condensation reaction using a basic functionality. Such a concerted reaction scheme may allow for the production of a greater amount of higher hydrocarbons to be formed for a given oxygenated intermediate feed.

[0094] In some embodiments, production of a >C4 compound may occur by condensation, which may include aldol condensation of the oxygenated intermediates in the presence of a condensation catalyst. Aldol-condensation generally involves the carbon-carbon coupling between two compounds, at least one of which may contain a carbonyl group, to form a larger organic molecule. For example, acetone may react with hydroxymethylfurfural to form a C9 species, which may subsequently react with another hydroxymethylfurfural molecule to form a C15 species. In various embodiments, the reaction is usually carried out in the presence of a condensation catalyst. The condensation reaction may be carried out in the vapor or liquid phase. In an embodiment, the reaction may take place at a temperature ranging from about 5° C. to about 375° C. depending on the reactivity of the carbonyl group.

[0095] The condensation catalyst will generally be a catalyst capable of forming longer chain compounds by linking two molecules through a new carbon-carbon bond, such as a basic catalyst, a multi-functional catalyst having both acid and base functionalities, or either type of catalyst also comprising an optional metal functionality. In some embodiments, the multi-functional catalyst may be a catalyst having both strong acid and strong base functionalities. In some embodiments, aldol catalysts may comprise 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 base catalyst may also comprise an oxide of Ti, Zr, V, Nb, Ta, Mo, Cr, W, Mn, Re, Al, Ga, In, Co, Ni, Si, Cu, Zn, Sn, Cd, Mg, P, Fe, or any combination thereof. In some embodiments, the condensation catalyst comprises mixed-oxide base catalysts. Suitable mixed-oxide base catalysts may comprise a combination of magnesium, zirconium, and oxygen, which may comprise, without limitation: 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. Different atomic ratios of Mg/Zr or the combinations of various other elements constituting the mixed oxide catalyst may be used ranging from about 0.01 to about 50. In some embodiments, the condensation catalyst may further include a metal or alloys comprising metals, such as 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. Such metals may be preferred when a dehydrogenation reaction is to be carried out in concert with the aldol condensation reaction. In some embodiments, preferred Group IA materials may include Li, Na, K, Cs and Rb. In some embodiments, preferred Group IIA materials may include Mg, Ca, Sr and Ba. In some embodiments, Group IIB materials may include Zn and Cd. In some embodiments, Group IIIB materials may include Y and La. Basic resins may include resins that exhibit basic functionality. The basic catalyst may be self-supporting or adhered to any one of the supports further described below, including supports containing carbon, silica, alumina, zirconia, titania, vanadia, ceria, nitride, boron nitride, heteropolyacids, alloys and mixtures thereof.

[0096] In one embodiment, the condensation catalyst may be derived from the combination of MgO and Al₂O₃ to form a hydrotalcite material. Another preferred material contains ZnO and Al₂O₃ in the form of a zinc aluminate spinel. Yet another preferred material is a combination of ZnO, Al₂O₃, and CuO. Each of these materials may also contain an addi-

tional metal function provided by a Group VIIIB metal, such as Pd or Pt. Such metals may be preferred when a dehydrogenation reaction is to be carried out in concert with the aldol condensation reaction. In some embodiments, the basic catalyst may be a metal oxide containing Cu, Ni, Zn, V, Zr, or mixtures thereof. In other embodiments, the basic catalyst may be a zinc aluminate metal containing Pt, Pd Cu, Ni, or mixtures thereof.

[0097] In some embodiments, a base-catalyzed condensation reaction may be performed using a condensation catalyst with both an acidic and a basic functionality. The acid-aldol condensation catalyst may comprise hydrotalcite, zinc-aluminate, phosphate, Li, Na, K, Cs, B, Rb, Mg, Si, Ca, Sr, Ba, Al, Ce, La, Sc, Y, Zr, Ti, Zn, Cr, or any combination thereof. In further embodiments, the acid-base 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 combinations thereof. In some embodiments, the acid-base catalyst may include a metal functionality provided by Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, alloys or combinations thereof. In some embodiments, the catalyst may further include Zn, Cd or phosphate. In some embodiments, the condensation catalyst may be a metal oxide containing Pd, Pt, Cu or Ni, and even more preferably an aluminate or zirconium metal oxide containing Mg and Cu, Pt, Pd or Ni. The acid-base catalyst may also include a hydroxyapatite (HAP) combined with any one or more of the above metals. The acid-base catalyst may be self-supporting or adhered to any one of the supports further described below, including supports containing carbon, silica, alumina, zirconia, titania, vanadia, ceria, nitride, boron nitride, heteropolyacids, alloys and mixtures thereof.

[0098] In some embodiments, the condensation catalyst may also include zeolites and 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 one embodiment, the condensation catalyst may be derived from the combination of MgO and Al₂O₃ to form a hydrotalcite material. Another preferred material may contain 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.

[0099] The condensation catalyst may be self-supporting (i.e., the catalyst does not need another material to serve as a support), or may require a separate support suitable for suspending the catalyst in the reactant stream. One exemplary support is silica, especially silica having a high surface area (greater than 100 square meters per gram), obtained by sol-gel synthesis, precipitation, or fuming. In other embodiments, particularly when the condensation catalyst is a powder, the catalyst system may include a binder to assist in forming the catalyst into a desirable catalyst shape. Applicable forming processes may include extrusion, pelletization, oil dropping, or other known processes. Zinc oxide, alumina, and a peptizing agent may also be mixed together and extruded to produce a formed material. After drying, this material may be calcined at a temperature appropriate for formation of the catalytically active phase. Other catalyst supports as known to one having ordinary skill in the art may also be used.

[0100] In some embodiments, a dehydration catalyst, a dehydrogenation catalyst, and the condensation catalyst may be present in the same reactor as the reaction conditions overlap to some degree. In these embodiments, a dehydration reaction and/or a dehydrogenation reaction may occur substantially simultaneously with the condensation reaction. In some embodiments, a catalyst may comprise active sites for a dehydration reaction and/or a dehydrogenation reaction in addition to a condensation reaction. For example, a catalyst may comprise active metals for a dehydration reaction and/or a dehydrogenation reaction along with a condensation reaction at separate sites on the catalyst or as alloys. Suitable active elements may comprise any of those listed above with respect to the dehydration catalyst, dehydrogenation catalyst, and the condensation catalyst. Alternately, a physical mixture of dehydration, dehydrogenation, and condensation catalysts may be employed. While not intending to be limited by theory, it is believed that using a condensation catalyst comprising a metal and/or an acid functionality may assist in pushing the equilibrium limited aldol condensation reaction toward completion. Advantageously, this may be used to effect multiple condensation reactions with dehydration and/or dehydrogenation of intermediates, in order to form (via condensation, dehydration, and/or dehydrogenation) higher molecular weight oligomers as desired to produce jet or diesel fuel.

[0101] The specific >C4 compounds produced in the condensation reaction may depend on various factors, including, without limitation, the type of oxygenated intermediates in the reactant stream, condensation temperature, condensation pressure, the reactivity of the catalyst, and the flow rate of the reactant stream. In general, the condensation reaction may be carried out at a temperature at which the thermodynamics of the proposed reaction are favorable. For condensed phase liquid reactions, the pressure within the reactor may be sufficient to maintain at least a portion of the reactants in the condensed liquid phase at the reactor inlet. For vapor phase reactions, the reaction may be carried out at a temperature where the vapor pressure of the oxygenates is at least about 0.1 bar, and the thermodynamics of the reaction are favorable. The condensation temperature will vary depending upon the specific oxygenated intermediates used, but may generally range between about 75° C. and about 500° C. for reactions taking place in the vapor phase, and more preferably range between about 125° C. and about 450° C. For liquid phase reactions, the condensation temperature may range between about 5° C. and about 475° C., and the condensation pressure may range between about 0.01 bar and about 100 bar. Preferably, the condensation temperature may range between about 15° C. and about 300° C., or between about 15° C. and 250° C.

[0102] Varying the factors above, as well as others, will generally result in a modification to the specific composition and yields of the >C4 compounds. For example, varying the temperature and/or pressure of the reactor system, or the particular catalyst formulations, may result in the production of >C4 alcohols and/or ketones instead of >C4 hydrocarbons. The >C4 hydrocarbon product may also contain a variety of olefins, and alkanes of various sizes (typically branched alkanes). Depending upon the condensation catalyst used, the hydrocarbon product may also include aromatic and cyclic hydrocarbon compounds. The >C4 hydrocarbon product may also contain undesirably high levels of olefins, which may lead to coking or deposits in combustion engines, or other

undesirable hydrocarbon products. In such cases, the hydrocarbons may optionally be hydrogenated to reduce the ketones to alcohols and hydrocarbons, while the alcohols and olefinic hydrocarbons may be reduced to alkanes, thereby forming a more desirable hydrocarbon product having reduced levels of olefins, aromatics or alcohols.

[0103] The condensation reactions 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 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 reactions.

[0104] In a continuous flow system, the reactor system may include an optional dehydrogenation bed adapted to produce dehydrogenated oxygenated intermediates, an optional dehydration bed adapted to produce dehydrated oxygenated intermediates, and a condensation bed adapted to produce >C4 compounds from the oxygenated intermediates. The dehydrogenation bed may be configured to receive the reactant stream and produce the desired oxygenated intermediates, which may have an increase in the amount of carbonyl-containing compounds. The dehydration bed may be configured to receive the reactant stream and produce the desired oxygenated intermediates. The condensation bed may be configured to receive the oxygenated intermediates for contact with the condensation catalyst and production of the desired >C4 compounds. For systems with one or more finishing steps, an additional reaction bed for conducting the finishing process or processes may be included after the condensation bed.

[0105] In some embodiments, the optional dehydration reaction, the optional dehydrogenation reaction, the optional ketonization reaction, the optional ring opening reaction, and the condensation reaction catalyst beds may be positioned within the same reactor vessel or in separate reactor vessels in fluid communication with each other. Each reactor vessel preferably may include an outlet adapted to remove the product stream from the reactor vessel. For systems with one or more finishing steps, the finishing reaction bed or beds may be within the same reactor vessel along with the condensation bed or in a separate reactor vessel in fluid communication with the reactor vessel having the condensation bed.

[0106] In some embodiments, the reactor system also may include additional outlets to allow for the removal of portions of the reactant stream to further advance or direct the reaction to the desired reaction products, and to allow for the collection and recycling of reaction byproducts for use in other portions of the system. In some embodiments, the reactor system also may include additional inlets to allow for the introduction of supplemental materials to further advance or direct the reaction to the desired reaction products, and to allow for the recycling of reaction byproducts for use in other reactions.

[0107] In some embodiments, the reactor system also may include elements which allow for the separation of the reactant stream into different components which may find use in different reaction schemes or to simply promote the desired reactions. For instance, a separator unit, such as a phase separator, extractor, purifier or distillation column, may be installed prior to the condensation step to remove water from the reactant stream for purposes of advancing the condensa-

tion reaction to favor the production of higher hydrocarbons. In some embodiments, a separation unit may be installed to remove specific intermediates to allow for the production of a desired product stream containing hydrocarbons within a particular carbon number range, or for use as end products or in other systems or processes. The condensation reaction may produce a broad range of compounds with carbon numbers ranging from C4 to C30 or greater. Exemplary compounds may include, for example, >C4 alkanes, >C4 alkenes, >C5 cycloalkanes, >C5 cycloalkenes, aryls, fused aryls, >C4 alcohols, >C4 ketones, and mixtures thereof. The >C4 alkanes and >C4 alkenes may range from 4 to about 30 carbon atoms (i.e. C4-C30 alkanes and C4-C30 alkenes) and may be branched or straight chain alkanes or alkenes. The >C4 alkanes and >C4 alkenes may also include fractions of C7-C14, C12-C24 alkanes and alkenes, respectively, with the C7-C14 fraction directed to jet fuel blends, and the C12-C24 fraction directed to diesel fuel blends and other industrial applications. Examples of various >C4 alkanes and >C4 alkenes may include, without limitation, butane, butene, pentane, pentene, 2-methylbutane, hexane, hexene, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, heptane, heptene, octane, octene, 2,2,4-trimethylpentane, 2,3-dimethyl hexane, 2,3,4-trimethylpentane, 2,3-dimethylpentane, nonane, nonene, decane, decene, undecane, undecene, dodecane, dodecene, tridecane, tridecene, tetradecane, tetradecene, pentadecane, pentadecene, hexadecane, hexadecene, heptyldecane, heptyldecene, octyldecane, octyldecene, nonyldecane, nonyldecene, eicosane, eicosene, uneicosane, uneicosene, doeicosane, doeicosene, trieicosane, trieicosene, tetraeicosane, tetraeicosene, and isomers thereof.

[0108] The >C5 cycloalkanes and >C5 cycloalkenes may have from 5 to about 30 carbon atoms and may be unsubstituted, mono-substituted or multi-substituted. In the case of mono-substituted and multi-substituted compounds, the substituted group may include a branched >C3 alkyl, a straight chain >C1 alkyl, a branched >C3 alkylene, a straight chain >C1 alkylene, a straight chain >C2 alkylene, an aryl group, or a combination thereof. In one embodiment, at least one of the substituted groups may include a branched C3-C12 alkyl, a straight chain C1-C12 alkyl, a branched C3-C12 alkylene, a straight chain C1-C12 alkylene, a straight chain C2-C12 alkylene, an aryl group, or a combination thereof. In yet other embodiments, at least one of the substituted groups may include a branched C3-C4 alkyl, a straight chain C1-C4 alkyl, a branched C3-C4 alkylene, a straight chain C1-C4 alkylene, a straight chain C2-C4 alkylene, an aryl group, or any combination thereof. Examples of desirable >C5 cycloalkanes and >C5 cycloalkenes may include, without limitation, cyclopentane, cyclopentene, cyclohexane, cyclohexene, methylcyclopentane, methylcyclopentene, ethylcyclopentane, ethylcyclopentene, ethylcyclohexane, ethylcyclohexene, and isomers thereof.

[0109] Aryl groups contain an aromatic hydrocarbon in either an unsubstituted (phenyl), mono-substituted or multi-substituted form. In the case of mono-substituted and multi-substituted compounds, the substituted group may include a branched >C3 alkyl, a straight chain >C1 alkyl, a branched >C3 alkylene, a straight chain >C2 alkylene, a phenyl group, or a combination thereof. In some embodiments, at least one of the substituted groups may include a branched C3-C12 alkyl, a straight chain C1-C12 alkyl, a branched C3-C12 alkylene, a straight chain C2-C12 alkylene, a phenyl group, or

any combination thereof. In yet other embodiments, at least one of the substituted groups may include a branched C3-C4 alkyl, a straight chain C1-C4 alkyl, a branched C3-C4 alkylene, a straight chain C2-C4 alkylene, a phenyl group, or any combination thereof. Examples of various aryl compounds may include, without limitation, benzene, toluene, xylene (dimethylbenzene), ethyl benzene, para-xylene, meta-xylene, ortho-xylene, and C9 aromatics.

[0110] Fused aryls contain bicyclic and polycyclic aromatic hydrocarbons, in either an unsubstituted, mono-substituted or multi-substituted form. In the case of mono-substituted and multi-substituted compounds, the substituted group may include a branched >C3 alkyl, a straight chain >C1 alkyl, a branched >C3 alkylene, a straight chain >C2 alkylene, a phenyl group, or a combination thereof. In other embodiments, at least one of the substituted groups may include a branched C3-C4 alkyl, a straight chain C1-C4 alkyl, a branched C3-C4 alkylene, a straight chain C2-C4 alkylene, a phenyl group, or any combination thereof. Examples of various fused aryls may include, without limitation, naphthalene, anthracene, tetrahydronaphthalene, and decahydronaphthalene, indane, indene, and isomers thereof.

[0111] The moderate fractions, such as C7-C14, may be separated for jet fuel, while heavier fractions, such as C12-C24, may be separated for diesel use. The heaviest fractions may be used as lubricants or cracked to produce additional gasoline and/or diesel fractions. The >C4 compounds may also find use as industrial chemicals, whether as an intermediate or an end product. For example, the aryls toluene, xylene, ethylbenzene, para-xylene, meta-xylene, and ortho-xylene may find use as chemical intermediates for the production of plastics and other products. Meanwhile, C9 aromatics and fused aryls, such as naphthalene, anthracene, tetrahydronaphthalene, and decahydronaphthalene, may find use as solvents in industrial processes.

[0112] In some embodiments, additional processes may be used to treat the fuel blend to remove certain components or further conform the fuel blend to a diesel or jet fuel standard. Suitable techniques may include hydrotreating to reduce the amount of or remove any remaining oxygen, sulfur, or nitrogen in the fuel blend. The conditions for hydrotreating a hydrocarbon stream will be known to one of ordinary skill in the art.

[0113] In some embodiments, hydrogenation may be carried out in place of or after the hydrotreating process to saturate at least some olefinic bonds. In some embodiments, a hydrogenation reaction may be carried out in concert with the aldol condensation reaction by including a metal functional group with the aldol condensation catalyst. Such hydrogenation may be performed to conform the fuel blend to a specific fuel standard (e.g., a diesel fuel standard or a jet fuel standard). The hydrogenation of the fuel blend stream may be carried out according to known procedures, either with the continuous or batch method. The hydrogenation reaction may be used to remove remaining carbonyl groups and/or hydroxyl groups. In such cases, any of the hydrogenation catalysts described above may be used. In general, the finishing step may be carried out at finishing temperatures ranging between about 80° C. and about 250° C., and finishing pressures may range between about 5 bar and about 150 bar. In some embodiments, the finishing step may be conducted in the vapor phase or liquid phase, and use, external hydrogen, recycled hydrogen, or combinations thereof, as necessary.

[0114] In some embodiments, isomerization may be used to treat the fuel blend to introduce a desired degree of branching or other shape selectivity to at least some components in the fuel blend. It may also be useful to remove any impurities before the hydrocarbons are contacted with the isomerization catalyst. The isomerization step may comprise an optional stripping step, wherein the fuel blend from the oligomerization reaction may be purified by stripping with water vapor or a suitable gas such as light hydrocarbon, nitrogen or hydrogen. The optional stripping step may be carried out in a countercurrent manner in a unit upstream of the isomerization catalyst, wherein the gas and liquid are contacted with each other, or before the actual isomerization reactor in a separate stripping unit utilizing countercurrent principle.

[0115] After the optional stripping step the fuel blend may be passed to a reactive isomerization unit comprising one or more catalyst beds. The catalyst beds of the isomerization unit may operate either in co-current or countercurrent manner. In the isomerization unit, the pressure may vary between about 20 bar to about 150 bar, preferably between about 20 bar to about 100 bar, the temperature ranging between about 195° C. and about 500° C., preferably between about 300° C. and about 400° C. In the isomerization unit, any isomerization catalyst known in the art may be used. In some embodiments, suitable isomerization catalysts may contain molecular sieve and/or a metal from Group VII and/or a carrier. In some embodiments, the isomerization catalyst may contain SAPO-11 or SAPO41 or ZSM-22 or ZSM-23 or ferrierite and Pt, Pd or Ni and Al₂O₃ or SiO₂. Typical isomerization catalysts may include, for example, Pt/SAPO-11/Al₂O₃, Pt/ZSM-22/Al₂O₃, Pt/ZSM-23/Al₂O₃ and Pt/SAPO-11/SiO₂.

[0116] Other factors, such as the concentration of water or undesired oxygenated intermediates, may also effect the composition and yields of the >C₄ compounds, as well as the activity and stability of the condensation catalyst. In such cases, the process may include a dewatering step that removes a portion of the water prior to the condensation reaction and/or the optional dehydration reaction, or a separation unit for removal of the undesired oxygenated intermediates. For instance, a separator unit, such as a phase separator, extractor, purifier or distillation column, may be installed prior to the condensation reactor so as to remove a portion of the water from the reactant stream containing the oxygenated intermediates. A separation unit may also be installed to remove specific oxygenated intermediates to allow for the production of a desired product stream containing hydrocarbons within a particular carbon range, or for use as end products or in other systems or processes.

[0117] Thus, in some embodiments, the fuel blend produced by the processes described herein may be a hydrocarbon mixture that meets the requirements for jet fuel (e.g., conforms with ASTM D1655). In other embodiments, the product of the processes described herein may be a hydrocarbon mixture that comprises a fuel blend meeting the requirements for a diesel fuel (e.g., conforms with ASTM D975).

[0118] In other embodiments, a fuel blend comprising gasoline hydrocarbons (i.e., a gasoline fuel) may be produced. "Gasoline hydrocarbons" refer to hydrocarbons predominantly comprising C₅-9 hydrocarbons, for example, C₆-8 hydrocarbons, and having a boiling point range from 32° C. (90° F.) to about 204° C. (400° F.). Gasoline hydrocarbons may include, but are not limited to, straight run gasoline, naphtha, fluidized or thermally catalytically

cracked gasoline, VB gasoline, and coker gasoline. Gasoline hydrocarbons content is determined by ASTM Method D2887.

[0119] In yet other embodiments, the >C₂ olefins may be produced by catalytically reacting the oxygenated intermediates in the presence of a dehydration catalyst at a dehydration temperature and dehydration pressure to produce a reaction stream comprising the >C₂ olefins. The >C₂ olefins may comprise straight or branched hydrocarbons containing one or more carbon-carbon double bonds. In general, the >C₂ olefins may contain from 2 to 8 carbon atoms, and more preferably from 3 to 5 carbon atoms. In some embodiments, the olefins may comprise propylene, butylene, pentylene, isomers of the foregoing, and mixtures of any two or more of the foregoing. In other embodiments, the >C₂ olefins may include >C₄ olefins produced by catalytically reacting a portion of the >C₂ olefins over an olefin isomerization catalyst.

[0120] The dehydration catalyst may comprise a member selected from the group consisting of an acidic alumina, aluminum phosphate, silica-alumina phosphate, amorphous silica-alumina, aluminosilicate, zirconia, sulfated zirconia, tungstated zirconia, tungsten carbide, molybdenum carbide, titania, sulfated carbon, phosphated carbon, phosphated silica, phosphated alumina, acidic resin, heteropolyacid, inorganic acid, and a combination of any two or more of the foregoing. In some embodiments, the dehydration catalyst may further comprise a modifier selected from the group consisting of Ce, Y, Sc, La, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, P, B, Bi, and a combination of any two or more of the foregoing. In other embodiments, the dehydration catalyst may further comprise an oxide of an element, the element selected from the group consisting 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 a combination of any two or more of the foregoing. In yet other embodiments, the dehydration catalyst may further comprise a metal selected from the group consisting of Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, an alloy of any two or more of the foregoing, and a combination of any two or more of the foregoing.

[0121] In yet other embodiments, the dehydration catalyst may comprise an aluminosilicate zeolite. In some embodiments, the dehydration catalyst may further comprise a modifier selected from the group consisting of Ga, In, Zn, Fe, Mo, Ag, Au, Ni, P, Sc, Y, Ta, a lanthanide, and a combination of any two or more of the foregoing. In some embodiments, the dehydration catalyst may further comprise a metal selected from the group consisting of Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, an alloy of any two or more of the foregoing, and a combination of any two or more of the foregoing.

[0122] In other embodiments, the dehydration catalyst may comprise a bifunctional pentasil ring-containing aluminosilicate zeolite. In some embodiments, the dehydration catalyst may further comprise a modifier selected from the group consisting of Ga, In, Zn, Fe, Mo, Ag, Au, Ni, P, Sc, Y, Ta, a lanthanide, and a combination of any two or more of the foregoing. In some embodiments, the dehydration catalyst may further comprise a metal selected from the group consisting of Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, an alloy of any two or more of the foregoing, and a combination of any two or more of the foregoing.

[0123] The dehydration reaction may be conducted at a temperature and pressure where the thermodynamics are

favorable. In general, the reaction may be performed in the vapor phase, liquid phase, or a combination of both. In some embodiments, the dehydration temperature may range between about 100° C. and about 500° C., and the dehydration pressure may range between about 1 bar (absolute) and about 60 bar. In some embodiments, the dehydration temperature may range between about 125° C. and about 450° C. In some embodiments, the dehydration temperature may range between about 150° C. and about 350° C., and the dehydration pressure may range between about 5 bar and about 50 bar. In some embodiments, the dehydration temperature may range between about 175° C. and about 325° C.

[0124] The >C6 paraffins may be produced by catalytically reacting >C2 olefins with a stream of >C4 isoparaffins in the presence of an alkylation catalyst at an alkylation temperature and alkylation pressure to produce a product stream comprising >C6 paraffins. The >C4 isoparaffins may include alkanes and cycloalkanes having 4 to 7 carbon atoms, such as isobutane, isopentane, naphthenes, and higher homologues having a tertiary carbon atom (e.g., 2-methylbutane and 2,4-dimethylpentane), isomers of the foregoing, and mixtures of any two or more of the foregoing. In some embodiments, the stream of >C4 isoparaffins may comprise internally generated >C4 isoparaffins, external >C4 isoparaffins, recycled >C4 isoparaffins, or combinations of any two or more of the foregoing.

[0125] The >C6 paraffins may be branched paraffins, but may also include normal paraffins. In one version, the >C6 paraffins may comprise a member selected from the group consisting of a branched C6-10 alkane, a branched C6 alkane, a branched C7 alkane, a branched C8 alkane, a branched C9 alkane, a branched C10 alkane, or a mixture of any two or more of the foregoing. In one version, the >C6 paraffins may include, for example, dimethylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane, methylpentane, 2-methylpentane, 3-methylpentane, dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, methylhexane, 2,3-dimethylhexane, 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, 2,2,3-trimethylpentane, 2,3,3-trimethylpentane, dimethylhexane, or mixtures of any two or more of the foregoing.

[0126] The alkylation catalyst may comprise a member selected from the group of sulfuric acid, hydrofluoric acid, aluminum chloride, boron trifluoride, solid phosphoric acid, chlorided alumina, acidic alumina, aluminum phosphate, silica-alumina phosphate, amorphous silica-alumina, aluminosilicate, aluminosilicate zeolite, zirconia, sulfated zirconia, tungstated zirconia, tungsten carbide, molybdenum carbide, titania, sulfated carbon, phosphated carbon, phosphated silica, phosphated alumina, acidic resin, heteropolyacid, inorganic acid, and a combination of any two or more of the foregoing. The alkylation catalyst may also include a mixture of a mineral acid with a Friedel-Crafts metal halide, such as aluminum bromide, and other proton donors.

[0127] In some embodiments, the alkylation catalyst may comprise an aluminosilicate zeolite. In some embodiments, the alkylation catalyst may further comprise a modifier selected from the group consisting of Ga, In, Zn, Fe, Mo, Ag, Au, Ni, P, Sc, Y, Ta, a lanthanide, and a combination of any two or more of the foregoing. In some embodiments, the alkylation catalyst may further comprise a metal selected from the group consisting of Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, an alloy of any two or more of the foregoing, and a combination of any two or more of the foregoing.

[0128] In some embodiments, the alkylation catalyst may comprise a bifunctional pentasil ring-containing aluminosilicate zeolite. In some embodiments, the alkylation catalyst may further comprise a modifier selected from the group consisting of Ga, In, Zn, Fe, Mo, Ag, Au, Ni, P, Sc, Y, Ta, a lanthanide, and a combination of any two or more of the foregoing. In some embodiments, the alkylation catalyst may further comprise a metal selected from the group consisting of Cu, Ag, Au, Pt, Ni, Fe, Co, Ru, Zn, Cd, Ga, In, Rh, Pd, Ir, Re, Mn, Cr, Mo, W, Sn, Os, an alloy of any two or more of the foregoing, and a combination of any two or more of the foregoing. In one version, the dehydration catalyst and the alkylation catalyst may be atomically identical.

[0129] The alkylation reaction may be conducted at a temperature where the thermodynamics are favorable. In general, the alkylation temperature may range between about -20° C. and about 300° C., and the alkylation pressure may range between about 1 bar (absolute) and about 80 bar. In some embodiments, the alkylation temperature may range between about 100° C. and about 300° C. In another version, the alkylation temperature may range between about 0° C. and about 100° C. In yet other embodiments, the alkylation temperature may range between about 0° C. and about 50° C. In still other embodiments, the alkylation temperature may range between about 70° C. and about 250° C., and the alkylation pressure may range between about 5 bar and about 80 bar. In some embodiments, the alkylation catalyst may comprise a mineral acid or a strong acid. In other embodiments, the alkylation catalyst may comprise a zeolite and the alkylation temperature may be greater than about 100° C.

[0130] In some embodiments, an olefinic oligomerization reaction may be conducted. The oligomerization reaction may be carried out in any suitable reactor configuration. Suitable configurations may include, but are not limited to, batch reactors, semi-batch reactors, or continuous reactor designs such as, for example, fluidized bed reactors with external regeneration vessels. Reactor designs may include, but are not limited to tubular reactors, fixed bed reactors, or any other reactor type suitable for carrying out the oligomerization reaction. In some embodiments, a continuous oligomerization process for the production of diesel and jet fuel boiling range hydrocarbons may be carried out using an oligomerization reactor for contacting an olefinic feed stream comprising short chain olefins having a chain length of from 2 to 8 carbon atoms with a zeolite catalyst under elevated temperature and pressure so as to convert the short chain olefins to a fuel blend in the diesel boiling range. The oligomerization reactor may be operated at relatively high pressures of about 20 bar to about 100 bar, and temperatures ranging between about 150° C. and about 300° C., preferably between about 200° C. to 250° C.

[0131] The resulting oligomerization stream results in a fuel blend that may have a wide variety of products including products comprising C5 to C24 hydrocarbons. Additional processing may be used to obtain a fuel blend meeting a desired standard. An initial separation step may be used to generate a fuel blend with a narrower range of carbon numbers. In some embodiments, a separation process such as a distillation process may be used to generate a fuel blend comprising C12 to C24 hydrocarbons for further processing. The remaining hydrocarbons may be used to produce a fuel blend for gasoline, recycled to the oligomerization reactor, or used in additional processes. For example, a kerosene fraction may be derived along with the diesel fraction and may either

be used as an illuminating paraffin, as a jet fuel blending component in conventional crude or synthetic derived jet fuels, or as reactant (especially C10 to C13 fraction) in the process to produce LAB (Linear Alkyl Benzene). The naphtha fraction, after hydroprocessing, may be routed to a thermal cracker for the production of ethylene and propylene or routed to a catalytic cracker to produce ethylene, propylene, and gasoline.

[0132] Additional processes may be used to treat the fuel blend to remove certain components or further conform the fuel blend to a diesel or jet fuel standard. Suitable techniques may include hydrotreating to remove any remaining oxygen, sulfur, or nitrogen in the fuel blend. Hydrogenation may be carried after the hydrotreating process to saturate at least some olefinic bonds. Such hydrogenation may be performed to conform the fuel blend to a specific fuel standard (e.g., a diesel fuel standard or a jet fuel standard). The hydrogenation step of the fuel blend stream may be carried out according to the known procedures, in a continuous or batchwise manner.

[0133] 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.

EXAMPLES

[0134] Unless otherwise indicated below, reactions were conducted in a Parr 5000 HASTELLOY multireactor unit containing 6×75 mL reactors operated in parallel at pressures up to 135 bar and temperatures up to 275° C., stirred by magnetic stir bar. Alternate studies were conducted in 100 mL Parr 4590 reactors, with mixing by a top-driven stir shaft impeller, which was also capable of attaining a pressure of 135 bar and a temperature of 275° C. Liquid chromatographic analyses were conducted by HPLC using a Bio-Rad Aminex HPX-87H column (300 mm×7.8 mm) at a flow rate of 0.6 mL/min 5 mM sulfuric acid in water and an oven temperature of 30° C. The run time was 70 minutes.

[0135] Gas chromatographic analyses were conducted using a 60 m×0.32 mm ID DB-5 column of 1 μm thickness, with 50:1 split ratio, 2 ml/min helium flow, and column oven temperature of 40° C. for 8 minutes, followed by a 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.

Example 1

[0136] Paste formation at high loadings of cellulosic biomass solids. 2.08 grams of finely ground pine wood sawdust containing 11.3% moisture was added to 25.5 grams of deionized water in a graduated cylinder. After mixing and allowing the wood to equilibrate, 10.4 grams of water was removed by syringe from the top of the wood bed. The cylinder was then tilted to decant additional water, but only one gram of additional water was removed, yielding a final water to dry solids ratio of 8.3:1. 0.1 grams of a slurry catalyst having a particle size of 1-25 microns was added, and the cylinder was mixed by inverting several times. Virtually no mixing of the slurry catalyst with the wood was observed due to paste formation by the finely divided wood.

Example 2

[0137] Role of biomass particulate size on digestion rate. Parallel Parr 5000 reactors were loaded with 20.0 grams of

50% 2-propanol in deionized water containing 0.05 grams of sodium carbonate. 2.70 grams of soft wood pine chips containing 39% moisture was added to each reactor. In the first reactor, a single 1 inch×1 inch×3 mm wood chip was added. In the second reactor, the pine wood was hand clipped to several ¼ inch×¼ inch×3 mm mini chips. In the third reactor, the pine wood was ground in a coffee grinder to a nominal 3 mm maximum size.

[0138] All three reactors were pressurized to 51 bar with H₂ and heated to 190° C. for one hour before ramping to 240° C. to complete a 5 hour cycle. The reactor contents were filtered by Whatman GF/F filter paper, and the paper with solids was dried in a vacuum oven overnight at 90° C. 78% by weight of wood from the first reactor dissolved, and the smaller wood chips in the other two reactors gave 72% by weight dissolution, on a water-free basis. It is believed that these results are essentially the same within experimental error and that the digestion rate is not significantly impacted by the wood chip size.

Example 3

[0139] Digestion of cellulosic biomass in the presence of a bottom-loaded slurry catalyst. The lower 2.25-inch zone of a 12.5 inch×0.5-inch O.D. (0.402-inch I.D.) digester tube was packed with ⅛-inch ceramic spheres (Denstone), followed by 0.7-inches of 14×40 mesh filter sand. On the sand was placed 0.604 grams of sulfided cobalt molybdate catalyst (DC2534, Criterion Catalyst & Technologies L.P) containing 1-10% cobalt oxide and molybdenum trioxide (up to 30 wt %) on alumina crushed to a particle size of less than 100 μm. The catalyst was previously sulfided as described in United States Patent Application publication 20100236988. The tube was then packed with 4.00 grams of southern pine wood chips having a nominal dimension of 3 mm×5 mm×5 mm, thereby forming an 8.7 inch chip bed.

[0140] The digestion unit was filled from the bottom with 50% 2-propanol/deionized water, buffered with 0.3 wt % sodium carbonate. Addition of the digestion solvent was continued until void spaces in the chip bed were filled and a liquid layer more than 0.5 inches above the bed was obtained. The ratio of solvent to dry wood in the packed bed was less than 5.8:1. Liquid flow was then terminated. The digestion unit was then pressured to 70 bar with H₂, and a continuous flow of hydrogen was added from the bottom of the digestion unit and vented from the top at a flow rate of 95 ml/min at standard room temperature and atmospheric pressure (STP). This flow rate corresponded to a superficial linear velocity of hydrogen flow of 0.05 cm/sec through the digestion unit. The bottom entry port was tubing having a nominal 3 mm O.D. (2 mm I.D.), thereby acting as a nozzle for gas bubble formation.

[0141] The digestion unit was then heated to 190° C. for 1.5 hours, followed by heating to 240° C. for 3.5 hours. At the end of the experiment, 9.24 grams of liquid product was drained from the digestion unit. 7.8 grams of condensed liquid product was also collected from overflow carried with the hydrogen sparge. Analysis of the liquid product indicated a mixture of oxygenated products (including monohydric alcohols and glycols) at 82% of the expected theoretical yield based on the amount of carbohydrates present in the initial wood charge. There were no remaining wood solids at the end of the digestion period.

Example 4

[0142] Digestion of cellulosic biomass in the presence of a top-loaded slurry catalyst. The experiment of Example 3 was

repeated, except the 0.600 grams of the catalyst was placed on top of the chip bed, rather than beneath it. The initial ratio of solvent to dry wood was less than 5.5:1. After digestion, 10.1 grams of liquid product was drained from the digestion unit, and 7.28 grams of condensed liquid product was collected from overflow. Again, no observable wood solids remained at the end of the digestion period. In contrast to catalyst loading beneath the chip bed, which produced a relatively high yield, the yield with catalyst loading on the top of the chip bed produced a yield that was only 28% of the theoretical yield. LC/MS analysis of the liquid product indicated the possible presence of oligomeric byproducts having a molecular weight greater than 300 and too high for detection by gas chromatography.

Example 5

[0143] Digestion of cellulosic biomass in the presence of a bottom-loaded slurry catalyst at a lower pressure. The experiment of Example 3 was repeated using 6.05 grams of southern pine chips and 15.4 mL of digestion solvent, added from the bottom, to fully cover the chip bed. In this case, the digestion unit was pressurized only to 37 bar, relative to an estimated solvent vapor pressure of about 32 bar. The vented hydrogen flow rate was 97 mL/min, and a digestion solvent of 50% 2-propanol in deionized water was co-fed from the bottom of the digestion unit at a flow rate of 0.05 mL/min. The digestion unit was heated to 190° C. for 1.5 hours, followed by heating to 240° C. for 5 hours, with hydrogen and digestion solvent flow rates maintained at the same levels. 18.53 grams of liquid product was drained from overflow, and 8.17 grams was drained from the digestion unit at the end of the run. 5.167 grams of wood chips were required to repack the digestion unit to its previous level. This result indicated a minimum of 85% digestion under the digestion conditions. Gas chromatographic analysis indicated only 31% conversion to the desired products. Comparison of this result with Example 3 showed that increased hydrogen pressure promoted stabilization of the soluble carbohydrates in the form of a higher yield.

Example 6

[0144] Digestion of cellulosic biomass in the presence of a bottom-loaded slurry catalyst with no hydrogen flow. The experiment of Example 5 was repeated with initial pressurization with 70 bar hydrogen, but only maintaining digestion solvent flow through the cellulosic biomass and no hydrogen flow. At the end of the run, 17.45 grams of liquid product was drained from overflow, and 7.4 grams of liquid product was drained from the digestion unit. 8 ml of undigested wood was also collected after the run, indicating about 50% conversion. Gas chromatographic analysis indicated about 27% yield of the desired reaction product in the liquid product. Again, poorer stabilization occurred when the amount of available hydrogen was reduced by termination of its flow.

Example 7

[0145] Digestion of cellulosic biomass in the absence of a slurry catalyst. The experiment of Example 3 was repeated after addition of 6.76 grams of pine chips, but without including the slurry catalyst. Although all the wood charge was digested in 6.5 hours, GC analysis indicated that only 3% of the desired reaction product formed.

Example 8

[0146] Digestion of cellulosic biomass in the presence of a bottom-loaded slurry catalyst at room temperature with gas and liquid flow. The experiment of Example 3 was repeated with the addition of 5.29 grams of southern pine wood chips, but the digestion unit was maintained at 23.5° C. for the duration of exposure. 7.597 grams of liquid product was drained from the digestion unit at the end of the run. Analysis of the chip bed following removal of the liquid product indicated uniform dispersal of the catalyst throughout the height of the cellulosic biomass bed, thereby showing that gas and liquid flow can be effective for distributing the slurry catalyst in the cellulosic biomass solids.

Example 9

[0147] Digestion of cellulosic biomass in the presence of a bottom-loaded slurry catalyst at room temperature with liquid flow only. The experiment of Example 8 was repeated after refilling with 7.13 grams of pine chips, except upflow of hydrogen was not used and only 0.05 mL/min upflow of the digestion solvent was present. 1.36 grams of liquid product was drained from overflow and 10.67 grams of liquid product was obtained from the digestion unit. Analysis of the chip bed following removal of the liquid product showed that the catalyst was only distributed in approximately the lower 20% of the chip bed, with no catalyst found distributed in the upper portions of the wood chip charge.

Example 10

[0148] Determination of minimum gas velocity needed for fluidization of slurry catalyst. A 100 mL graduated cylinder was filled with 1 gram of nominal 1-25 μ m NiMo/alumina slurry catalyst and 50 grams of deionized water. A fritted sparging stone (ACE Glass) was placed at the bottom of the graduated cylinder and connected to an N₂ supply using 1/8-inch Teflon tubing. The N₂ flow rate was varied to determine minimum flow rate needed to completely fluidize the slurry catalyst to the top of the liquid column. The linear velocity of gas corresponding to complete fluidization determined using this method was 0.037 cm/sec. Hydrogen gas flow, when used in the previous examples, exceeded this minimum velocity for fluidization and suspension of the catalyst.

[0149] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods may also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with

a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles “a” or “an,” as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

We claim:

1. A biomass conversion system comprising:
a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular hydrogen;
an optional hydrogen feed line that is operatively connected to the hydrothermal digestion unit; and
a fluid circulation loop comprising the hydrothermal digestion unit and a catalytic reduction reactor unit, the catalytic reduction reactor unit also containing the slurry catalyst.
2. The biomass conversion system of claim 1, wherein the fluid circulation loop is configured to establish upward fluid flow in the hydrothermal digestion unit.
3. The biomass conversion system of claim 1, further comprising:
a retention mechanism within the hydrothermal digestion unit that is operable to retain cellulosic biomass solids having a particle size of about 3 mm or above.
4. The biomass conversion system of claim 1, further comprising:
a reaction product takeoff line in fluid communication with the fluid circulation loop, the reaction product takeoff line being located between the hydrothermal digestion unit and an outlet of the catalytic reduction reactor unit.
5. The biomass conversion system of claim 4, further comprising:
a solids separation mechanism that is operatively connected to the reaction product takeoff line.
6. The biomass conversion system of claim 1, wherein the slurry catalyst comprises a poison-tolerant catalyst.
7. The biomass conversion system of claim 1, wherein the slurry catalyst is regenerable through exposure to water having a temperature of at least about 200° C.

8. The biomass conversion system of claim 1, wherein the slurry catalyst is operable to generate molecular hydrogen.

9. The biomass conversion system of claim 1, further comprising:

a solids introduction mechanism that is operatively connected to the hydrothermal digestion unit, the solids introduction mechanism comprising an atmospheric pressure zone and a pressure transition zone that cycles between atmospheric pressure and a higher pressure state.

10. The biomass conversion system of claim 1, wherein the fluid circulation loop is configured to establish upward fluid flow in the catalytic reduction reactor unit.

11. A method comprising:

providing cellulosic biomass solids in a hydrothermal digestion unit that contains a slurry catalyst capable of activating molecular hydrogen;

heating the cellulosic biomass solids in the hydrothermal digestion unit in the presence of molecular hydrogen while circulating the slurry catalyst therethrough, thereby forming a hydrolysate comprising soluble carbohydrates within a liquor phase;

at least partially transforming the soluble carbohydrates into a reaction product while the soluble carbohydrates are within the hydrothermal digestion unit; and

transferring at least a portion of the liquor phase to a catalytic reduction reactor unit that also contains the slurry catalyst, so as to further transform the soluble carbohydrates into the reaction product.

12. The method of claim 11, further comprising:

recirculating at least a portion of the liquor phase from the catalytic reduction reactor unit to the hydrothermal digestion unit.

13. The method of claim 11, further comprising:

after further transforming the soluble carbohydrates into the reaction product, withdrawing a portion of the reaction product from the catalytic reduction reactor unit; and

converting the reaction product into a biofuel.

14. The method of claim 13, further comprising:

separating solids from the reaction product after withdrawing.

15. The method of claim 11, further comprising:

further forming the reaction product in the catalytic reduction reactor unit.

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