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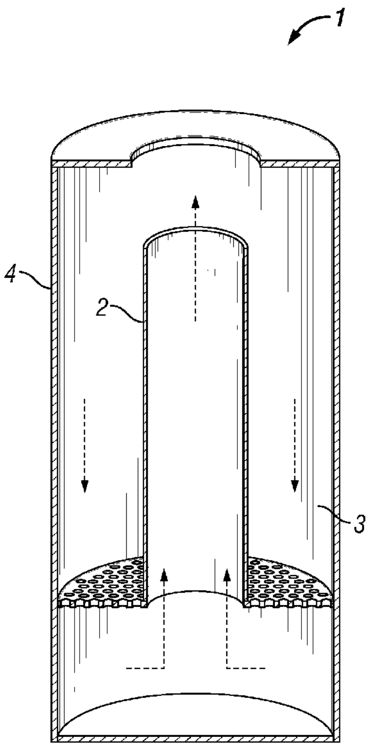

FIG. 1

(57) Abstract: Digestion of cellulosic biomass solids may be conducted in a pressure vessel that contains both a hydrothermal digestion unit and a catalytic reduction reactor unit. Biomass conversion systems incorporating such a feature may comprise: a pressure vessel that comprises a first section comprising a hydrothermal digestion unit and a second section comprising a first catalytic reduction reactor unit that contains a first catalyst capable of activating molecular hydrogen; wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another; a biomass feed mechanism that is operatively connected to the pressure vessel, the biomass feed mechanism being capable of introducing cellulosic biomass solids to the pressure vessel and also capable of withdrawing a reaction product from the first catalytic reduction reactor unit; and a hydrogen feed line that is operatively connected to the first catalytic reduction reactor unit.

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BIOMASS CONVERSION SYSTEM HAVING A SINGLE-VESSEL HYDROTHERMAL DIGESTION UNIT AND A CATALYTIC REDUCTION REACTOR UNIT FOR INTEGRATED STABILIZATION OF A HYDROLYSATE AND METHOD FOR USE THEREOF

Field of the Invention

The present disclosure generally relates to digestion of cellulosic biomass solids, and, more specifically, to biomass conversion systems and methods for use thereof that allow a hydrolysate comprising soluble carbohydrates to be catalytically transformed into a more stable reaction product using a pressurized vessel that contains a fluidly coupled hydrothermal digestion unit and a catalytic reduction reactor unit.

Background of the Invention

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.

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 is co-present with the cellulose can make its processing difficult, as discussed hereinafter.

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 components 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). Energy- and cost-efficient processes for processing cellulosic biomass into fuel blends having similar compositions to fossil fuels would be highly desirable to address the foregoing issues and others.

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 cellulosic biomass may be converted into a more usable form. However, fermentation processes are typically slow, require large volume reactors and high dilution conditions, 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.

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.

Production of soluble carbohydrates for use in fuel blends and other materials via routine modification of paper and pulpwood digestion processes is not believed to be economically 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, particularly over extended periods of time. Once produced by digestion, soluble carbohydrates are very reactive and can rapidly degrade to produce caramelans and other heavy ends degradation products, especially under higher temperature conditions, such as above 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.

One way in which soluble carbohydrates can be protected from thermal degradation is through subjecting them to one or more catalytic reduction reactions, which may include hydrogenation and/or hydrogenolysis reactions. Stabilizing soluble carbohydrates 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. Depending on the reaction conditions and catalyst used, reaction products formed as a result of conducting one or more catalytic reduction reactions on soluble carbohydrates may include triols, diols, monohydric alcohols, or any combination thereof, some of which may also include a residual carbonyl functionality (e.g., an aldehyde or ketone). Such reaction products may be more thermally stable than soluble carbohydrates and are readily transformable into fuel blends and other materials through conducting one or more downstream reforming reactions. In addition, the foregoing types of reaction products are good solvents in which a hydrothermal digestion may be performed, thereby promoting solubilzation of soluble carbohydrates as their reaction products and cellulosic biomass components such as lignin, for example.

Another issue associated with the processing of cellulosic biomass into fuel blends and other materials 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 gradually decreases to the point that they can 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.

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. In addition to catalyst poisons, lignin, which is a non-cellulosic biopolymer, may become solubilized in conjunction with the production of soluble carbohydrates. If not addressed in some manner, lignin concentrations may become sufficiently high during biomass conversion that precipitation eventually occurs, thereby resulting in costly system downtime. In the alternative, some lignin may remain unsolubilized, and costly system downtime may eventually be needed to affect its removal.

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

The present disclosure generally relates to digestion of cellulosic biomass solids, and, more specifically, to biomass conversion systems and methods for use thereof that allow a hydrolysate comprising soluble carbohydrates to be catalytically transformed into a more stable reaction product using a pressurized vessel that contains a fluidly coupled hydrothermal digestion unit and a catalytic reduction reactor unit.

In some embodiments, the present invention provides biomass conversion systems comprising: a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first catalyst capable of activating molecular hydrogen; wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another; a biomass feed mechanism that is operatively connected to the pressure vessel, the biomass feed mechanism being capable of introducing cellulosic biomass solids to the pressure vessel and also capable of withdrawing a reaction product from the first catalytic reduction reactor unit; and a hydrogen feed line that is operatively connected to the first catalytic reduction reactor unit.

In some embodiments, the present invention provides biomass conversion systems comprising: a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first catalyst capable of activating molecular hydrogen; wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another; a biomass feed mechanism that is operatively connected to the pressure vessel, the biomass feed mechanism being capable of introducing cellulosic biomass solids to the pressure vessel while the pressure vessel maintains a pressurized state; a hydrogen feed line that is operatively connected to the first catalytic reduction reactor unit; and a fluid circulation loop comprising the pressure vessel and a second catalytic reduction reactor unit that contains a second catalyst capable of activating molecular hydrogen.

In some embodiments, the present invention provides methods comprising: providing a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first catalyst capable of activating molecular hydrogen (first hydrocatalytic catalyst); wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another; adding cellulosic biomass solids to the pressure vessel; heating the cellulosic biomass solids in the hydrothermal digestion unit of the pressure vessel, thereby forming a hydrolysate comprising soluble carbohydrates within a liquor phase; conveying the liquor phase through the first catalytic reduction reactor unit in the presence of molecular hydrogen so as to at least partially transform the soluble carbohydrates into a reaction product; and conveying at least a portion of the liquor phase from the pressure vessel to a second catalytic reduction reactor unit that contains a second catalyst capable of activating molecular hydrogen (second hydrocatalytic catalyst), so as to further transform the soluble carbohydrates into the reaction product.

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 Drawings

The following figures are included to illustrate certain aspects of the present disclosure, and should not be viewed as exclusive embodiments. 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.

FIGURE 1 shows a schematic of an illustrative annular pressure vessel containing an inner catalytic reduction reactor unit and an outer hydrothermal digestion unit housed within an outer pressure housing.

FIGURE 2 shows a schematic of an illustrative pressure vessel in which a hydrothermal digestion unit and a catalytic reduction reactor unit are located alongside one another within an outer pressure housing.

FIGURE 3 shows a schematic of an illustrative biomass conversion system having a hydrothermal digestion unit and a catalytic reduction reactor unit housed within a pressure vessel.

FIGURE 4 shows a schematic of an illustrative biomass conversion system having a hydrothermal digestion unit and a catalytic reduction reactor unit housed within a pressure vessel in which a fluid circulation loop establishes direct fluid communication between a fluid inlet and a fluid outlet of the pressure vessel.

Detailed Description

The present disclosure generally relates to digestion of cellulosic biomass solids, and, more specifically, to biomass conversion systems and methods for use thereof that allow a hydrolysate comprising soluble carbohydrates to be catalytically transformed into a more stable reaction product using a pressurized vessel that contains a fluidly coupled hydrothermal digestion unit and a catalytic reduction reactor unit.

In the embodiments described herein, the digestion rate of cellulosic biomass may be accelerated in the presence of a digestion solvent at elevated temperatures and pressures that maintain the digestion solvent in a liquid state above its normal boiling point. The more rapid rate of digestion may be desirable from the standpoint of throughput, but soluble carbohydrates may be susceptible to degradation under these conditions, as discussed in more detail hereinafter. In various embodiments, the digestion solvent may contain an organic solvent, particularly an in situ-generated organic solvent, which may provide certain advantages, as described hereinafter.

The present disclosure provides systems and methods that allow cellulosic biomass solids to be efficiently digested to form soluble carbohydrates, which may subsequently be converted through one or more catalytic reduction reactions (e.g., hydrogenolysis and/or hydrogenation) into more stable reaction products comprising oxygenated intermediates that may be further processed into higher hydrocarbons. The higher hydrocarbons may be useful in forming industrial chemicals and transportation fuels (i.e., a biofuel), including, for example, synthetic gasoline, diesel fuels, jet fuels, and the like. As used herein, the term “biofuel” will refer to any transportation fuel formed from a biological source. Such biofuels may be referred to herein as “fuel blends.” In particular, the systems and methods described herein are configured such that cellulosic biomass solids can be digested to produce a hydrolysate that comprises soluble carbohydrates, where at least a portion of the soluble carbohydrates in the hydrolysate may be quickly transformed into a more stable reaction product following digestion through a catalytic reduction reaction before degradation has had an opportunity to take place. In the embodiments described herein, the foregoing is accomplished by fluidly coupling a hydrothermal digestion unit and a catalytic reduction reactor unit together in a pressure vessel. Various configurations for the fluidly coupled hydrothermal digestion unit and catalytic reduction reactor unit are possible, as described hereinafter. Several types of catalysts that are capable of activating molecular hydrogen (also referred to herein as "hydrogen-activating catalysts" or "hydrocatalytic catalyst") may be used to mediate the catalytic reduction reaction. Advantageously, the cellulosic biomass solids may be used to promote retention of the catalyst within the pressure vessel, as described hereinafter. Converting the soluble carbohydrates into a more stable reaction product nearer their point of origin may reduce the amount of thermal decomposition that occurs following hydrothermal digestion, thereby increasing yields of the desired reaction product and promoting high biomass conversion rates. Other advantages may also be realized by conducting hydrothermal digestion and catalytic reduction within a single pressure vessel, as discussed hereinafter.

As used herein, the term "oxygenated intermediates" refers to alcohols, polyols, ketones, aldehydes, and mixtures thereof that are produced from a catalytic reduction reaction (e.g., hydrogenolysis and/or hydrogenation) of soluble carbohydrates. As used herein, the term "higher hydrocarbons" refers to hydrocarbons having an oxygen to carbon ratio less than that of at least one component of the biomass source from which they are produced. As used herein, the term "hydrocarbon" refers to an organic compound comprising primarily hydrogen and carbon, although heteroatoms such as oxygen, nitrogen, sulfur, and/or phosphorus may be present in some embodiments. Thus, the term "hydrocarbon" also encompasses heteroatom-substituted compounds containing carbon, hydrogen, and oxygen, for example.

When a digestion solvent is used at high temperatures and pressures in a hydrothermal digestion, the digestion process may become fairly energy intensive. If the energy input requirements for the digestion process become too great, the economic feasibility of cellulosic biomass as a feedstock material may be jeopardized. That is, if the energy input needed to digest cellulosic biomass becomes too great, processing costs may become higher than the actual value of the product being generated. In order to keep processing costs low, the amount of externally added heat input to the digestion process is desirably kept as low as possible while achieving as high as possible conversion of the cellulosic biomass into soluble carbohydrates, which can subsequently be transformed into a more stable reaction product. Conversion of soluble carbohydrates into a more stable reaction product is described in more detail hereinafter.

In the embodiments described herein, the soluble carbohydrates may be at least partially stabilized by a catalytic reduction reaction that takes place within the same pressure vessel in which hydrothermal digestion occurs. Once the soluble carbohydrates have been at least partially transformed into a more stable reaction product, completion of the conversion of the soluble carbohydrates into the reaction product may take place in a separate catalytic reduction reactor unit that is not contained within the pressure vessel. 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.

A number of advantages may be realized by conducting hydrothermal digestion and catalytic reduction within the same pressure vessel, as in the embodiments described herein. As discussed above, a leading advantage of the biomass conversion systems described herein is that the systems are configured to rapidly stabilize a significant fraction of the hydrolysate produced in the hydrothermal digestion unit. Stabilization of the hydrolysate may be accomplished by at least partially converting the soluble carbohydrates in the hydrolysate into a reaction product through a catalytic reduction reaction that takes place in a catalytic reduction reactor unit that is fluidly coupled to the hydrothermal digestion unit. By fluidly coupling the hydrothermal digestion unit and the catalytic reduction reactor unit together in a single pressure vessel, transit times of the hydrolysate to the catalytic reduction reactor unit may be lowered, thereby decreasing the opportunity for the soluble carbohydrates to degrade.

Another significant advantage of the presently described biomass conversion systems is that conducting hydrothermal digestion and catalytic reduction in a single pressure vessel may allow excellent heat integration and heat management to be realized. As described hereinafter, hydrothermal digestion is an endothermic process, whereas catalytic reduction is an exothermic process. Since the two processes occur within the same pressure vessel in the biomass conversion systems described herein, the excess heat generated by the catalytic reduction reaction may be used to drive the hydrothermal digestion process. This can improve the overall energy efficiency of the biomass conversion process by limiting the amount of external energy needing to be input to drive the hydrothermal digestion.

As discussed above, the initial reaction product produced in the pressure vessel may be conveyed to a second catalytic reduction reactor unit for further transformation into a reaction product that is more amenable to being transformed into a biofuel or other material. The second catalytic reduction reactor unit in which the further transformation takes place may be separate from the pressure vessel in which the initial catalytic reduction reaction takes place. The further transformation that takes place 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. The reaction product obtained from the second catalytic reduction reactor unit may be recirculated to the pressure vessel, where it may serve as a digestion solvent, and/or it may be withdrawn from the second catalytic reduction reactor unit for subsequent conversion into a biofuel or other material. By at least partially transforming the soluble carbohydrates into a reaction product before the hydrolysate reaches the second catalytic reduction reactor unit, demands on the second 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 second catalytic reduction reactor unit than would otherwise be feasible, since at least a portion of the soluble carbohydrates have already been transformed prior to reaching the second catalytic reduction reactor unit. Furthermore, since significant heat integration efficiency may be realized by conducting hydrothermal digestion and the initial catalytic reduction reaction in the same pressure vessel, there may be a reduced need to recirculate the reaction product from the second catalytic reduction reactor unit to the pressure vessel 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. The foregoing factors may also reduce capital and operational costs associated with the biomass conversion systems.

In further regard to heat integration efficiency, the present biomass conversion systems may also be particularly advantageous, since the pressure vessel of the systems may be continuously maintained at elevated temperatures and pressures, in some embodiments. Thus, hydrothermal digestion may take place continuously as long as fresh cellulosic biomass solids can be continuously or semi-continuously supplied to the pressure vessel without depressurization taking place. Without the ability to introduce fresh cellulosic biomass solids to the pressure vessel while maintaining a pressurized state, depressurization and cooling 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 biomass is added to a vessel in a substantially uninterrupted manner without full depressurization taking place. 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 vessel without full depressurization taking place. A further description of biomass feed mechanisms that may supply biomass to a pressurized vessel are described in more detail below.

In the embodiments described herein, various types of fluidly mobile catalysts that are capable of activating molecular hydrogen may be used in the catalytic reduction reactor unit present within the pressure vessel. As described hereinafter, at least some cellulosic biomass solids may also be present in the catalytic reduction reactor unit of the pressure vessel. Therefore, catalysts that are susceptible to plugging in the presence of solids, such as fixed bed catalysts, for example, are not typically used in this location. Illustrative types of catalysts that may be used in the catalytic reduction reactor unit of the pressure vessel include, for example, slurry catalysts, ebullating bed catalysts, fluidized bed catalysts, and the like. The same catalyst or a different catalyst may be present in the second catalytic reduction reactor unit that is not located within the pressure vessel.

A common problem associated with the use of fluidly mobile catalysts is that suitable containment mechanisms (e.g., catalyst screens, filters, and the like) are often needed in order to maintain the catalysts in a desired location. In the embodiments described herein, however, it has been discovered that cellulosic biomass solids may be advantageously used to help maintain the fluidly mobile catalyst within the pressure vessel and/or to provide a mechanism by which the catalyst may be easily returned to the pressure vessel during biomass addition thereto. Specifically, it has been discovered that an agglomeration of cellulosic biomass solids may effectively sequester catalyst solids to limit the free movement of the catalyst. Thus, not only are the cellulosic biomass solids digested in the pressure vessel, but they also may effectively serve as a catalyst screen in the pressure vessel and/or in a biomass feed mechanism used for introducing the cellulosic biomass solids to the pressure vessel. In some embodiments, the cellulosic biomass solids may be processed to a size that is more effective for screening the catalyst, before being added to the pressure vessel, if desired. Moreover, free movement of the fluidly mobile catalyst through the cellulosic biomass solids is advantageous to promote distribution of the catalyst, thereby leading to more ready stabilization of soluble carbohydrates.

In a similar manner to that which occurs for catalyst sequestration, as described above, the biomass conversion systems described herein may aid in reducing the amount of cellulosic biomass fines transported from the pressure vessel to the second catalytic reduction reactor unit. The cellulosic biomass fines may be natively present in the biomass introduced to the pressure vessel or produced in the course of the biomass undergoing hydrothermal digestion. Thus, a fluidly mobile catalyst can be used in the second catalytic reduction reactor unit, in some embodiments, or a fixed bed catalyst can be used in the second catalytic reduction reactor unit, in other embodiments. Optionally, a solids separation mechanism may also be used to sequester any catalyst and/or cellulosic biomass fines in the liquor phase being conveyed to the second catalytic reduction reactor unit in order to confer additional protection thereto.

The biomass conversion systems and associated methods described herein are to be further distinguished from those of the paper and pulpwood industry, where the goal is to harvest partially digested wood pulp, rather than obtaining as high as possible a quantity of soluble carbohydrates, which can be subsequently converted into a reaction product comprising oxygenated intermediates. Since the goal of paper and pulpwood processing is to obtain raw wood pulp, such digestion processes may be conducted at lower temperatures and pressures to remove lower quantities of soluble carbohydrates and non-cellulosic components from the biomass, which can be removed at lower temperatures. In some embodiments described herein, at least 60% of the cellulosic biomass, on a dry basis, may be digested to produce a hydrolysate comprising soluble carbohydrates. In other embodiments described herein, at least 90% of the cellulosic biomass, on a dry basis, may be digested to produce a hydrolysate comprising soluble carbohydrates. Given the intent of paper and pulpwood processing, it is anticipated that much lower quantities of soluble carbohydrates are produced in these processes. The design of the present biomass conversion systems may enable such high conversion rates by minimizing the formation of degradation products during the processing of cellulosic biomass, while maintaining long residence times during hydrothermal digestion.

Although conducting a combined hydrothermal digestion of cellulosic biomass solids and a catalytic reduction reaction of soluble carbohydrates in a single pressure vessel may be advantageous from the standpoint of stabilizing soluble carbohydrates and achieving excellent heat integration, biomass conversion systems implementing such configurations may present several challenges, as discussed above. Catalyst poisoning may also be an issue for some catalysts, since there is little to no opportunity to remove catalyst poisons from the hydrolysate when catalytic reduction is conducted in the same pressure vessel as the hydrothermal digestion. One way in which this issue can be circumvented is to use a poison-tolerant catalyst, some of which are discussed hereinbelow. Another alternative is to use a catalyst that is regenerable upon exposure to conditions that can be established in the pressure vessel. For example, in some embodiments, a slurry catalyst may be regenerated through exposure to water at a temperature of at least 300°C.

Another alternative to address the issue of catalyst poisoning is to conduct the digestion of the cellulosic biomass solids in stages using separate digestion units. Many of the poisons that may deactivate a catalyst arise from sulfur-containing compounds and nitrogen-containing compounds in the raw cellulosic biomass solids. These compounds, along with at least some hemicellulose and lignins, may be at least partially removed from cellulosic biomass solids at lower digestion temperatures than those at which cellulose produces soluble carbohydrates. By controlling the digestion temperature, a biomass pulp may be produced that is enriched in cellulose but depleted in catalyst poisons, hemicellulose, and/or lignins, none of which are desirably present in a process for producing soluble carbohydrates or a reaction product derived therefrom. Advantageously, the catalyst poisons, hemicellulose, and/or lignins can be at least partially removed from the biomass pulp before it is added to the pressure vessel and processed to produce a reaction product, as described in the embodiments herein. That is, in some embodiments, a biomass pulp that has been at least partially depleted in catalyst poisons, hemicellulose, and/or lignins may be introduced to the pressure vessel described herein.

Not only may the use of multiple digestion units lessen the likelihood of catalyst poisoning, but such use also may advantageously reduce the likelihood of lignin precipitation from the liquor phase and formation of undesirable blockages in the biomass conversion systems (e.g., in transfer lines and the like). In some embodiments, the biomass conversion systems described herein may further comprise a separation mechanism for lignin. By removal of at least some of the lignin from the cellulosic biomass solids before hydrothermal digestion takes place, separation of the lignin from the liquor phase may be conducted less frequently than would otherwise be possible.

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 digestion in the embodiments described herein. The cellulosic biomass solids may also be present in a slurry form in the embodiments described herein.

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 bluestream, 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.

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 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.

In some embodiments, biomass conversion systems described herein can comprise: a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first catalyst capable of activating molecular hydrogen; wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another; a biomass feed mechanism that is operatively connected to the pressure vessel, the biomass feed mechanism being capable of introducing cellulosic biomass solids to the pressure vessel and also capable of withdrawing a reaction product from the first catalytic reduction reactor unit; and a hydrogen feed line that is operatively connected to the first catalytic reduction reactor unit.

In some embodiments, the biomass conversion systems may further comprise a fluid circulation loop that establishes fluid communication between a fluid inlet of the pressure vessel and a fluid outlet of the biomass feed mechanism. That is, in such embodiments, the biomass conversion systems may be configured such that a liquor phase may be transported through the biomass feed mechanism and subsequently returned to the pressure vessel. In other embodiments, the fluid circulation loop may establish fluid communication directly between a fluid inlet and a fluid outlet of the pressure vessel. That is, in such embodiments, the liquor phase need not necessarily pass through the biomass feed mechanism. Once returned to the pressure vessel, reaction product in the liquor phase may serve as a digestion solvent in the hydrothermal digestion unit and/or unreacted soluble carbohydrates therein may undergo further catalytic reduction to produce a reaction product. In addition, as described above, the liquor phase returned to the pressure vessel may aid in maintaining its thermal profile.

In some embodiments, the fluid circulation loop may further comprise a second catalytic reduction reactor unit that contains a second catalyst capable of activating molecular hydrogen. As described above, the second catalytic reduction reactor unit may be used to further transform the soluble carbohydrates within the liquor phase into a reaction product. In some embodiments, the first catalyst and the second catalyst may be the same. In other embodiments, the first catalyst and the second catalyst may be different. Further description of suitable catalysts for the catalytic reduction reactor units follows below.

In some embodiments, biomass conversion systems described herein can comprise: a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first catalyst capable of activating molecular hydrogen; wherein the hydrothermal digestion unit and the first catalytic reduction reactor are in fluid communication with one another; a biomass feed mechanism that is operatively connected to the pressure vessel, the biomass feed mechanism being capable of introducing cellulosic biomass solids to the pressure vessel while the pressure vessel maintains a pressurized state; a hydrogen feed line that is operatively connected to the first catalytic reduction reactor unit; and a fluid circulation loop comprising the pressure vessel and a second catalytic reduction reactor unit that contains a second catalyst capable of activating molecular hydrogen.

Various configurations for the pressure vessel having a separated hydrothermal digestion unit and a catalytic reduction reactor unit are possible. In some embodiments, the pressure vessel may comprise an annular structure, with the first section comprising an outer portion of the annular structure, and the second section comprising an inner portion of the annular structure. That is, in such embodiments, the biomass conversion systems may comprise an inner first catalytic reduction reactor unit and an outer hydrothermal digestion unit, all maintained within an exterior pressure housing. In other embodiments, the first section and the second section may be located alongside one another in the pressure vessel. Other configurations for the pressure vessel may be possible, and, in general, any pressure vessel having a hydrothermal digestion unit and a catalytic reduction reactor unit that are fluidly connected to, but separated from, one another may be used in the present embodiments.

FIGURES 1 and 2 show schematics of illustrative pressure vessels containing a hydrothermal digestion unit and a catalytic reduction reactor unit, which are fluidly connected to, but separated from, one another. FIGURE 1 shows a schematic of an illustrative annular pressure vessel 1 containing an inner catalytic reduction reactor unit 2 and an outer hydrothermal digestion unit 3 housed within outer pressure housing 4. FIGURE 2 shows a schematic of an illustrative pressure vessel 5 in which a hydrothermal digestion unit 6 and a catalytic reduction reactor unit 7 are located alongside one another within outer pressure housing 8. Although FIGURES 1 and 2 have depicted the pressure vessel as having a substantially cylindrical configuration, it is to be recognized that any shape can be used. The arrows in FIGURES 1 and 2 represent the flow direction of hydrolysate and bulk biomass during digestion and that of the liquor phase as it passes through the catalytic reduction reactor unit in the process of being transformed into a reaction product. As depicted in FIGURES 1 and 2, catalytic reduction reactor units 2 and 7 are operated as gas lift, slurry, or ebullating bed reactors. However, other reactor configurations may also be used. The foregoing pressure vessels may be used in conjunction with the biomass conversion systems described herein. FIGURES 3 and 4, which are discussed in more detail hereinbelow, show illustrative biomass conversion systems having a hydrothermal digestion unit and a catalytic reduction reactor unit housed within a pressure vessel.

In some embodiments, the biomass conversion systems may comprise a biomass feed mechanism that is operatively connected to the pressure vessel. In some embodiments, the biomass feed mechanism may be capable of introducing cellulosic biomass solids to the pressure vessel while the pressure vessel maintains a pressurized state. In some embodiments, the biomass feed mechanism may also be capable of withdrawing a reaction product from the pressure vessel. In various embodiments, the biomass feed mechanism may comprise a pressure transition zone that cycles between a lower pressure state (e.g., atmospheric pressure) and a higher pressure state. In some further embodiments, the biomass feed mechanism may further comprise an atmospheric pressure zone. Cellulosic biomass solids may be introduced to the pressure transition zone, and their pressure may be increased to a level suitable for being introduced to the pressure vessel.

When present, suitable atmospheric pressure zones of the biomass feed mechanism 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 pressure vessel 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.

In some embodiments, the biomass feed mechanism may allow cellulosic biomass solids to be introduced to the pressure vessel without the pressure vessel being fully depressurized. Pressurizing the cellulosic biomass solids prior to introduction to the pressure vessel may allow the hydrothermal digestion unit to remain pressurized and operating continuously. Pressurization can help maintain heat integration and energy efficiency of the biomass digestion process, as described above. Additional benefits of pressurizing the cellulosic biomass solids are also discussed hereinafter.

In some embodiments, pressurization of the cellulosic biomass solids within the biomass feed mechanism may take place, at least in part, by introducing at least a portion of the liquor phase in the pressure vessel 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.

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 solids, which may cause the biomass solids to sink in the digestion solvent once introduced to the pressure vessel. 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 solids up to temperature once introduction to the pressure vessel takes place. Both of these features may improve the efficiency of the digestion process.

FIGURE 3 shows a schematic of an illustrative biomass conversion system having a hydrothermal digestion unit and a catalytic reduction reactor unit housed within a pressure vessel. For conciseness, FIGURE 3 has been depicted with the annular pressure vessel configuration depicted in FIGURE 1. However, it is to be recognized that other pressure vessel configurations may be used in the embodiments described herein. Moreover, the catalytic reduction reactor unit housed within the pressure vessel has been shown in cut-away form so that the cellulosic biomass solids and catalyst particles therein may be more clearly depicted.

As shown in FIGURE 3, biomass conversion system 10 includes pressure vessel 12, which contains hydrothermal digestion unit 14 and first catalytic reduction reactor unit 16 within outer pressure housing 18. Hydrothermal digestion unit 14 and first catalytic reduction reactor unit 16 are fluidly coupled to one another by fluid conduit region 26. Fluid conduit region 26 allows a hydrolysate produced within hydrothermal digestion unit 14 to flow downward by gravity and thereafter be transported upward within first catalytic reduction reactor unit 16 in the presence of molecular hydrogen. As depicted in FIGURE 3, first catalytic reduction reactor unit 16 operates, at least in part, by gas lift.

Cellulosic biomass solids may be introduced to pressure vessel 12 by biomass introduction mechanism 20, which comprises atmospheric pressure zone 22 and pressure transition zone 24. Cellulosic biomass solids may be housed in atmospheric pressure zone 22 and added, as needed, to pressure transition zone 24. Cellulosic biomass solids added to pressure transition zone 24 may be cycled from atmospheric pressure to an elevated pressure state such that they may be introduced to pressure vessel 12. There may be various valves or other pressure isolation mechanisms present between atmospheric pressure zone 22 and pressure transition zone 24 and between pressure transition zone 24 and pressure vessel 12, which have not been depicted for purposes of clarity. Suitable pressure isolation mechanisms and use thereof will be familiar to one having ordinary skill in the art. Suitable biomass feed mechanisms that may supply cellulosic biomass solids to a pressurized vessel are described in further detail hereinabove.

During operation of biomass conversion system 10, addition of cellulosic biomass solids to pressure vessel 12 may occur on a continuous or semi-continuous basis. As described above, cellulosic biomass solids may be added to biomass feed mechanism 20 and raised to an elevated pressure state. Thereafter, the cellulosic biomass solids may be introduced to pressure vessel 12. When introduced to pressure vessel 12, the cellulosic biomass solids may enter hydrothermal digestion unit 14 and undergo at least partial transformation into soluble carbohydrates. In some embodiments, at least a portion of the cellulosic biomass solids may also enter first catalytic reduction reactor unit 16. As described hereinafter, the introduction of cellulosic biomass solids to first catalytic reduction reactor unit 16 may be particularly advantageous.

Hydrolysate produced in hydrothermal digestion unit 14 may drain into fluid conduit region 26, where it may subsequently enter first catalytic reduction reactor unit 16 and flow upward therethrough in the course of being transformed into a reaction product. Molecular hydrogen may be introduced to first catalytic reduction reactor unit 16 via hydrogen feed line 28. First catalytic reduction reactor unit 16 contains catalyst particles 30 and optionally cellulosic biomass solids 32. As described above, cellulosic biomass solids 32 may aid in retaining catalyst particles 30 within first catalytic reduction reactor unit 16. Some of the catalyst particles not retained by first catalytic reduction reactor unit 16 may be conveyed by the downward biomass and hydrolysate flow within hydrothermal digestion unit 14. These catalyst particles may be returned to first catalytic reduction reactor unit 16 during the flow of hydrolysate thereto, as described above.

As depicted in FIGURE 3, fluid circulation loop 40 establishes fluid communication between a fluid inlet 42 of pressure vessel 12 and a fluid outlet 44 of biomass feed mechanism 20. Optionally, the fluid circulation loop can establish a direct fluid connection between a fluid outlet and a fluid inlet of pressure vessel 12. For example, in some embodiments, fluid circulation loop 40 may establish a direct fluid connection between fluid outlet 46 of pressure vessel 12 and fluid inlet 42 of pressure vessel 12 (see FIGURE 4). As depicted in FIGURE 3, fluid circulation loop 40 also contains second catalytic reduction reactor unit 50 where further transformation of the hydrolysate may occur. Fluid circulation loop 40 may be configured to establish countercurrent flow in hydrothermal digestion unit 14 once liquor phase therein is recirculated to pressure vessel 12. Other flow motifs, including co-current flow, are also possible. Reaction product that is not returned to pressure vessel 12 may be withdrawn from fluid circulation loop 40 by reaction product takeoff line 64 for further processing.

During operation of biomass conversion system 10, there may be an open fluid connection between pressure vessel 10 and biomass feed mechanism 20, such that liquor phase may flow into pressure transition zone 24. Reaction product produced in first catalytic reduction reactor unit 16 may exit pressure vessel 12 via biomass feed mechanism 20 (i.e. by fluid circulation loop 40, which is operatively connected to pressure transition zone 24). Catalyst particles 30 not retained within first catalytic reduction reactor unit 16 or returned thereto by bulk biomass and hydrolysate flow may become sequestered within cellulosic biomass solids housed within pressure transition zone 24. Once these cellulosic biomass solids are introduced to pressure vessel 12, the catalyst particles may also be returned thereto. Thus, by flowing the liquor phase from pressure vessel 12 through cellulosic biomass solids in pressure transition zone 24, an even more effective retention of catalyst may be realized.

In some embodiments, it may be desirable that the liquor phase does not flow through pressure transition zone 24, at least temporarily. For example, when fresh cellulosic biomass solids are being added to pressure transition zone 24, the pressure transition zone may be at atmospheric pressure, in which case it may be isolated from pressure vessel 12 by a pressure isolation mechanism, as discussed above. In such cases, flow within fluid circulation loop 40 may be maintained by routing the liquor phase through bypass line 48, which establishes direct fluid communication to pressure vessel 12 via fluid outlet 46.

In some embodiments, the fluid circulation loop may directly connect to pressure vessel 12, rather than connecting to pressure transition zone 24 of biomass feed mechanism 20. Although the benefit of flowing the liquor phase through the cellulosic biomass solids in pressure transition zone 24 is lost in such embodiments, this configuration represents a viable alternative configuration for the fluid connection of fluid circulation loop 40. FIGURE 4 shows a schematic of an illustrative biomass conversion system having a hydrothermal digestion unit and a catalytic reduction reactor unit housed within a pressure vessel in which a fluid circulation loop establishes direct fluid communication between a fluid inlet and a fluid outlet of the pressure vessel. Features in FIGURE 4 have identical reference characters to those depicted in FIGURE 3 and described hereinabove. For conciseness, these features will not be described again in detail.

Although the foregoing description has described the benefits afforded by using cellulosic biomass solids to sequester catalyst particles, it is to be recognized that conventional catalyst screens and filters may be used to retain the catalyst within first catalytic reduction reactor unit 14, second catalytic reduction reactor unit 50, or both. Such catalyst screens and filters will 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 25% or less by volume, may also be deployed as catalytic filters to separate slurry catalyst from a liquid filtrate. External filters such 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, leave 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.

Various optional elements may also be present within the biomass conversion systems described herein. In some embodiments, there may be a solids separation mechanism 60 within fluid circulation loop 40. Use of a solids separation mechanism may protect second catalytic reduction reactor unit 50 from plugging by catalyst particles and cellulosic biomass fines, for example. Suitable solids separation mechanisms are described in more detail hereinbelow. In some embodiments, there may be a phase separation mechanism 62 within fluid circulation loop 40. Phase separation mechanism 62 may be used to at least partially separate an organic phase from an aqueous of the reaction product exiting second catalytic reduction reactor unit 50. Suitable phase separation mechanisms are also discussed in more detail hereinbelow.

In various embodiments, suitable materials for the pressure vessel may include, for example, carbon steel, stainless steel, or a similar alloy. In some embodiments, the pressure vessel may be capable of maintaining a pressure of at least 30 bar. In some embodiments, the pressure vessel may be capable of maintaining a pressure of at least 60 bar. In some embodiments, the pressure vessel may be capable of maintaining a pressure of at least 90 bar.

Various catalysts may be used in conjunction with the catalytic reduction reactor units described herein. In some embodiments, the catalyst in the first catalytic reduction reactor unit and the second catalytic reduction reactor unit may be the same. In other embodiments, they may be different. In some embodiments, the catalyst in the first catalytic reduction reactor unit may comprise a slurry catalyst, an ebullating bed catalyst, or a fluidized bed catalyst. In some embodiments, the catalyst in the second catalytic reduction reactor unit may comprise a fixed bed catalyst, a slurry catalyst, an ebullating bed catalyst, or a fluidized bed catalyst. In some embodiments, the first catalyst, the second catalyst, or both may comprise a slurry catalyst.

In some embodiments, the first catalyst, the second catalyst, or both may comprise a poison-tolerant catalyst. Use of a poison-tolerant catalyst may be particularly desirable when catalyst poisons are not removed from the liquor phase of the hydrolysate before catalytic reduction takes 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 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.

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, and 2013/0109896. Sulfiding may take place by treating a catalyst with hydrogen sulfide or other sulfiding agent, 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 may give a high yield of oxygenated intermediates, while not forming an excess amount of C2 – C4 alkanes. The oxygenated intermediates 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. Use of a poison-tolerant catalyst may lessen the need to perform stepwise digestion or a purification of the hydrolysate (e.g., by ion-exchange) prior to the catalytic reduction reaction taking place. Even when catalyst poisons are removed from the hydrolysate, a poison-tolerant catalyst may still be used to lessen process downtime.

In some embodiments, the catalyst may be regenerable. In some embodiments, the catalyst may be a regenerable slurry catalyst. For example, in some embodiments, a 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 200°C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least 250°C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least 300°C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least 350°C. In some embodiments, the slurry catalyst may be regenerated through exposure to water having a temperature of at least 400°C. Exposure to water in a subcritical state or a supercritical state may be used for regeneration of the catalyst. Regeneration of the slurry catalyst may take place at any location in the biomass conversion system, but more typically, regeneration takes place in one of the catalytic reduction reactor units while hydrolysate is not being processed therein. Most catalysts effective for mediating a catalytic reduction reaction are also regenerable, at least in part, through thermal treatments with hydrogen. A particularly suitable slurry catalyst that can be regenerated though 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. Another suitable slurry catalyst may be a platinum or a palladium compound disposed on a solid support.

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.

In some embodiments, the fluid circulation loop may be configured to establish countercurrent flow in the hydrothermal digestion unit of the pressure vessel. As used herein, the term “countercurrent flow” refers to the direction a reaction product enters the hydrothermal digestion unit relative to the direction of bulk biomass flow in the hydrothermal digestion unit. Other flow configurations such as, for example, co-current flow may also be used, if desired.

In some embodiments, there may be a solids separation mechanism located within the fluid circulation loop between a fluid outlet of the biomass feed mechanism and a fluid inlet of the second catalytic reduction reactor unit. In some embodiments, there may be a solids separation mechanism located within the fluid circulation loop between a fluid outlet of the pressure vessel and a fluid inlet of the second catalytic reduction reactor unit. A solids separation mechanism in this location may be used to protect the second catalytic reduction reactor unit and reduce the likelihood of plugging. Solids separation mechanisms may include 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 within the fluid circulation loop, where at least one of the filters may be backflushed to the hydrothermal digestion unit while forward fluid flow continues through at least some of the remaining filters and onward to the catalytic reduction reactor unit. That is, two or more filters may be operated in a reciprocating manner. In some embodiments, one or more hydroclones may be used within the fluid circulation loop. Use of filters and hydroclones within the fluid circulation loop are described in commonly owned United States Patent Application Publications 2013/0152456 and 2013/0158308.

In some embodiments, there may be a phase separation mechanism within the fluid circulation loop between a fluid outlet of the second catalytic reduction reactor unit and a fluid inlet of the pressure vessel. Suitable phase separation mechanisms and techniques are discussed in more detail below.

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 a fluid inlet of the pressure vessel and a fluid outlet of the second 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. Suitable solids separation mechanisms may include those described previously.

In some embodiments, methods for processing cellulosic biomass solids are described herein. In some embodiments, methods for processing cellulosic biomass solids can comprise: providing a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first catalyst capable of activating molecular hydrogen; wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another; adding cellulosic biomass solids to the pressure vessel; heating the cellulosic biomass solids in the hydrothermal digestion unit of the pressure vessel, thereby forming a hydrolysate comprising soluble carbohydrates within a liquor phase; conveying the liquor phase through the first catalytic reduction reactor unit in the presence of molecular hydrogen so as to at least partially transform the soluble carbohydrates into a reaction product; and conveying at least a portion of the liquor phase from the pressure vessel to a second catalytic reduction reactor unit that contains a second catalyst capable of activating molecular hydrogen, so as to further transform the soluble carbohydrates into the reaction product.

In some embodiments, the cellulosic biomass solids may be added to the pressure vessel while the pressure vessel maintains a pressurized state. In some embodiments, the pressure vessel may be maintained at a pressure of at least 30 bar while the cellulosic biomass solids are being added. In some embodiments, the cellulosic biomass solids may be added to the pressure vessel from a biomass feed mechanism, where the biomass feed mechanism is capable of introducing cellulosic biomass solids to the pressure vessel while the pressure vessel maintains a pressurized state. Pressure vessels suitable for the foregoing purpose have been set forth above. In some embodiments, the biomass feed mechanism may add at least some cellulosic biomass solids to the hydrothermal digestion unit of the pressure vessel. In some or other embodiments, the biomass feed mechanism may add at least some cellulosic biomass solids to the first catalytic reduction reactor unit of the pressure vessel.

In some embodiments, the methods may further comprise conveying the liquor phase to the second catalytic reduction reactor unit through the biomass feed mechanism. In some embodiments, the biomass feed mechanism may be empty while conveying the liquor phase. In other embodiments, the biomass feed mechanism may contain cellulosic biomass solids while the liquor phase is being conveyed therethrough. As described above, cellulosic biomass solids in the biomass feed mechanism may be used to sequester catalyst solids thereon and limit their transportation to the second catalytic reduction reactor unit. Catalyst solids sequestered on the cellulosic biomass solids within the biomass feed mechanism may be returned to the pressure vessel during subsequent additions of cellulosic biomass solids thereto.

In some embodiments, the methods may further comprise conveying the liquor phase to the second catalytic reduction reactor unit without the liquor phase passing through a biomass feed mechanism. For example, the liquor phase may pass directly from a fluid outlet on the pressure vessel to a fluid inlet on the second catalytic reduction reactor unit. In some embodiments, direct transfer of the liquor phase may take place when the biomass feed mechanism is at atmospheric pressure and being loaded with additional cellulosic biomass solids. In other embodiments, the biomass feed mechanism may be bypassed entirely. For example, if catalyst solids are effectively retained within the pressure vessel it may be possible for the biomass feed mechanism to be bypassed when the liquor phase is being conveyed to the second catalytic reduction reactor unit.

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 of the pressure vessel prior to pressurization. In other embodiments, washing may occur before the biomass is placed in the pressure vessel. For example, in some embodiments, the biomass may be washed in a biomass feed mechanism before pressurization takes place.

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, 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 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.

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 catalytic reduction reactor units. 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.

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 100°C to 250°C for a period of time. In some embodiments, the period of time may range between 0.25 hours and 24 hours. In some embodiments, the digestion to produce soluble carbohydrates may occur at a pressure ranging between 1 bar (absolute) and 100 bar. In some embodiments, the digestion process may be conducted in stages, with a first stage being conducted at 160°C or below to solubilize and convert hemicellulose into a reaction product, and with a second stage being conducted at 160°C or above to solubilize and convert cellulose into a reaction product. The lower temperature digestion may also remove at least some catalyst poisons and lignin from the cellulosic biomass solids.

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

In some embodiments, the methods may further comprise withdrawing at least a portion of the reaction product from the biomass conversion system. For example, in some embodiments, the methods may further comprise withdrawing a portion of the reaction product from a fluid outlet of the second catalytic reduction reactor unit, after further transforming the soluble carbohydrates into reaction product. 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 from the liquor phase as it is being conveyed to the second catalytic reduction reactor unit, as described above.

In some embodiments, the methods may further comprise recirculating at least a portion of the liquor phase from the second catalytic reduction reactor unit to the pressure vessel. Recirculation of the liquor phase from the second catalytic reduction reactor unit to the pressure vessel may, for example, help regulate temperature therein, provide makeup digestion solvent for the digestion process, and the like. Recirculation from the second catalytic reduction reactor unit to the pressure vessel 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 pressure vessel (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).

A particular benefit of performing hydrothermal digestion and catalytic reduction in the same pressure vessel 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 pressure vessel, given than an exothermic catalytic reduction reaction is already taking place therein. Accordingly, a relatively high proportion of the liquor phase exiting the second 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. Additionally, lower recycle ratios may help promote retention of the catalyst within the pressure vessel and lessen the demands on the cellulosic biomass solids to retain the catalyst therein. 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 second catalytic reduction reactor unit to the pressure vessel at a recycle ratio ranging between 0.2 and 10. In some embodiments, the liquor phase may be recirculated from the second catalytic reduction reactor unit to the pressure vessel at a recycle ratio ranging between 1 and 10, or between 1 and 5, or between 0.2 and 2, or between 0.5 and 2, or between 1 and 2, or between 0.2 and 1, or between 0.5 and 1. In some embodiments, the liquor phase may be recirculated from the second catalytic reduction reactor unit to the pressure vessel at a recycle ratio of 2 or less. In some embodiments, the liquor phase may be recirculated from the second catalytic reduction reactor unit to the pressure vessel at a recycle ratio of 1 or less. In some embodiments, the liquor phase may be recirculated from the second catalytic reduction reactor unit to the pressure vessel such that countercurrent 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.

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

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, at least 60% of the cellulosic biomass solids, on a dry basis, may be digested to produce hydrolysate. In some embodiments, at least 70% of the cellulosic biomass solids, on a dry basis, may be digested to produce hydrolysate. In some embodiments, at least 80% of the cellulosic biomass solids, on a dry basis, may be digested to produce hydrolysate. In some embodiments, at least 90% of the cellulosic biomass solids, on a dry basis, may be digested to produce hydrolysate.

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

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 second 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.

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 and depicted in FIGURES 3 and 4, a liquor phase containing the reaction product may be recirculated to the pressure vessel 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, alkylation reactions, and the like. A description of the initial hydrogenolysis reaction and the further catalytic reforming reactions are described hereinafter.

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

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.

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 110°C to 300°C, and preferably from 170°C to 300°C, and most preferably from 180°C to 290°C.

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

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

In some embodiments, the reaction products of the hydrogenolysis reaction may comprise greater than 25% by mole, or alternatively, greater than 30% by mole of polyols, which may result in a greater conversion to a biofuel in a subsequent processing reaction.

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.

A second aspect of hydrogenolysis entails the breaking of -OH bonds such as: $RC(H)_2\text{-}OH + H_2 \rightarrow RCH_3 + H_2O$. 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.

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.

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 >C4 hydrocarbon; and (7) any combination thereof. Acid catalyzed condensations may similarly entail optional hydrogenation or dehydrogenation reactions, dehydration, and oligomerization reactions. Additional polishing reactions may also be used to conform the product to a specific fuel standard, including reactions conducted in the presence of hydrogen and a hydrogenation catalyst to remove functional groups from final fuel product. 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.

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.

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 C8 and C16. Wide-cut or naphtha-type Airplane fuel (including Jet B) typically has a carbon number distribution between C5 and C15. A fuel blend meeting ASTM D1655 may be defined as jet fuel.

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.

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.

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.

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, hydroxylmethylfurfural, 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.

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, H_2SO_4), solid acids (e.g., zeolites, ion-exchange resins) and acid salts (e.g., $LaCl_3$). 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.

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-pyrollidone (NMP), and any combination thereof. Other suitable aprotic solvents may also be used alone or in combination with any of these solvents.

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.

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.

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 5°C to 375°C depending on the reactivity of the carbonyl group.

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 0.01 to 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.

In one embodiment, the condensation catalyst may be derived from the combination of MgO and Al_2O_3 to form a hydrotalcite material. Another preferred material contains ZnO and Al_2O_3 in the form of a zinc aluminate spinel. Yet another preferred material is a combination of ZnO, Al_2O_3, and CuO. Each of these materials may also contain an additional 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.

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.

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 Al_2O_3 to form a hydrotalcite material. Another preferred material may contain a combination of MgO and ZrO_2, or a combination of ZnO and Al2O3. Each of these materials may also contain an additional metal function provided by copper or a Group VIIIB metal, such as Ni, Pd, Pt, or combinations of the foregoing.

The condensation 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.

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.

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 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 75°C and 500°C for reactions taking place in the vapor phase, and more preferably range between 125oC and 450°C. For liquid phase reactions, the condensation temperature may range between 5°C and 475°C, and the condensation pressure may range between 0.01 bar and 100 bar. Preferably, the condensation temperature may range between 15°C and 300°C, or between 15°C and 250°C.

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.

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.

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.

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.

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.

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 condensation 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 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.

The >C5 cycloalkanes and >C5 cycloalkenes may have from 5 to 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.

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.

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.

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.

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.

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 80°C and 250°C, and finishing pressures may range between 5 bar and 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.

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.

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 20 bar to 150 bar, preferably between 20 bar to 100 bar, the temperature ranging between 195°C and 500°C, preferably between 300°C and 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 Al_2O_3 or SiO_2. Typical isomerization catalysts may include, for example, Pt/SAPO-11/Al_2O_3, Pt/ZSM-22/Al_2O_3, Pt/ZSM-23/Al_2O_3 and Pt/SAPO-11/SiO_2.

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.

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).

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 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.

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.

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.

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.

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.

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 100°C and 500°C, and the dehydration pressure may range between 1 bar (absolute) and 60 bar. In some embodiments, the dehydration temperature may range between 125°C and 450°C. In some embodiments, the dehydration temperature may range between 150°C and 350°C, and the dehydration pressure may range between 5 bar and 50 bar. In some embodiments, the dehydration temperature may range between 175°C and 325°C.

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.

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.

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.

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.

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.

The alkylation reaction may be conducted at a temperature where the thermodynamics are favorable. In general, the alkylation temperature may range between t -20°C and 300°C, and the alkylation pressure may range between 1 bar (absolute) and 80 bar. In some embodiments, the alkylation temperature may range between 100°C and 300°C. In another version, the alkylation temperature may range between 0°C and 100°C. In yet other embodiments, the alkylation temperature may range between 0°C and 50°C. In still other embodiments, the alkylation temperature may range between 70°C and 250°C, and the alkylation pressure may range between 5 bar and 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 100°C.

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 20 bar to 100 bar, and temperatures ranging between 150°C and 300°C, preferably between 200°C to 250°C.

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.

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.

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

Batch reaction studies were conducted in a Parr5000 Hastelloy multi-reactor having 6 x 75-milliliter reactors operated in parallel at pressures up to 135 bar and temperatures up to 275°C, stirred by magnetic stir bar.

Example 1: Determination of minimum gas velocity needed for fluidization of a slurry catalyst. A 100 mL graduated cylinder was filled with 1 gram of nominal 1 – 25 μm nickel-molybdenum/alumina slurry catalyst and 50 grams of deionized water, maintained at 23°C and atmospheric pressure. 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 linear velocity needed to completely fluidize the slurry catalyst to the top of the liquid column. The linear velocity of gas corresponding to complete fluidization and mixing of slurry to the top of the liquid level was 0.037 cm/sec.

Example 2: Digestion of cellulosic biomass solids. A 1 inch diameter x 12 inch tall digester-reactor tube was fitted with a 0.5 inch diameter annular draft tube insert. The insert was centered via welding two 1.16 inch x 1.5 cm tabs at 2 cm from each end. Two 1 cm high x 6 mm V-shaped slots were cut diametrically opposed in the bottom of the tube to allow unhindered flow of solid and liquid from the outer annulus to the inside draft tube. A nominal 0.89 inch diameter metal plate was installed in the bottom of the one inch O.D. tube, to retain the inner annulus and prevent solids from dropping into pipe and tube fittings used at the bottom of the digester-reactor. A 1/8 inch stainless steel gas dispersion tube was inserted from the bottom, up through the bottom plate, and extending 0.5 inches into the annular draft tube to a position of 1 cm above the top of the v-shaped bottom slots. The draft tube extended to within 3.5 inches of the top overflow port on the digester-reactor tube, such that liquid and gas flow through the inner annulus could spill over and return to the bottom of the assembly via the outer annulus, once a driving force of gas flow through the inner annulus was established.

The digester-reactor was charged with 0.762 grams of nominal 1 – 25 micron nickel-molybdenum/alumina slurry catalyst, added to the bottom and retained by the metal plate. The inner annulus was packed with 4.794 grams of southern pine mini chips (39% moisture) having a nominal size of 6 mm x 5 mm x 3 mm. Two plugs of glass wool totaling 0.035 grams were placed diametrically opposed in the outer annulus, 3 cm from top of inner annulus, to capture a portion of circulating solids in the digester-reactor system.

The digester-reactor was filled with solvent (45% by weight 1,2-propylene glycol, 5% ethylene glycol in deionized water with 0.05 wt. % potassium carbonate buffer), to a level of 1.5 inches above the top of the inner annulus. Hydrogen flow was introduced at the bottom of the digester-reactor, and routed to a high pressure product vessel maintained at 70 bar via pressure regulator, before venting at 94 mL/min at atmospheric pressure and room temperature (23°C). The calculated superficial linear velocity through the draft tube was 0.049 cm/sec, which exceeded the minimum linear velocity for complete mixing of slurry catalyst in Example 1. In the absence of the draft tube, the linear gas velocity was only 0.013 cm/sec, or less than one-third of that needed for complete mixing and suspension of slurry catalyst to take place. The digester-reactor was then heated via band heaters (Gaumer) to 190°C. After 1.5 hours, temperature was ramped to 230°C for 2 hours, followed by an increase to 250°C for 3 hours for a total run time of 6.5 hours.

Measurement of the remaining wood chip height at the end of the run indicated 59% digestion of the wood chips. ICP analysis of the solids, which were retained on the glass wool plugs extracted from the outer annulus after the run, indicated the presence of nickel and molybdenum, corresponding to 2.2 and 2.9 wt. % catalyst present on the two filter plugs. This result indicated that nickel-molybdate catalyst was lifted from the bottom of the draft tube to the upper portion of the outer annulus via the motive force of gas sparging.

Product formation (mono-oxygenates, glycols, diols, alkanes, and acids) was monitored by gas chromatograph. Gas chromatographic analyses were conducted using a 60 m x 0.32 mm ID DB-5 column of 1 μm thickness, with 50:1 split ratio, 2 mL/min helium flow, and column oven 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.

Analysis of collected liquid drained from the digester-reactor indicated 1.68 wt. % product formation for components elutable from the GC at an injector temperature of 375°C, whereby all eluted components exhibited a retention time less than sorbitol, a C6 sugar alcohol. This corresponds to an expected value of 1.66 wt. % product formation, if all hemicellulose and cellulose carbohydrates were selectively converted to liquid products of sufficiently small molecular weight to elute from the GC. Yields to desired product were thus 102% of those expected for selective conversion of carbohydrates to lower molecular weight intermediates.

Examples 3 - 5: Impact of catalyst on yields. In Example 3, the digester-reactor was charged with 20.0 grams of 50 wt. % 2-propanol in deionized water, 0.30 grams of sodium carbonate buffer, and 0.504 grams of a sulfided cobalt-molybdate catalyst (DC2534, Criterion Catalyst & Technologies L.P containing 1–10% cobalt oxide and molybdenum trioxide (up to 30 wt. %) on alumina, and less than 2% nickel) that was crushed to less than 100 microns in size. The catalyst was previously sulfided as described in United States Patent Application publication 20100236988. The reactor was then charged with 2.7 grams of southern pine wood chips containing 39% moisture, ground via knife mill, before pressuring with 50 – 51 bar of H2, and heating to 240°C for 5 hours with stirring. The cycle was repeated for three additions of wood chips.

After cooling and venting of pressure, a liquid sample was withdrawn for analysis by GC. The reactor contents were filtered through Whatman GF/F filter paper, and the paper with solids was dried in a vacuum oven overnight at 90ºC to assess undigested solids. GC analysis indicated the presence of 6.3 wt. % of desired intermediates, oxygenated components having a retention time less than that of sorbitol. This value corresponded to an estimated 79% yield of target intermediates relative to the mass of carbohydrates charged as wood to the reactor, or a selectivity of 90% relative to the 88% digestion of wood charged.

For Example 4, the experiment was repeated with 3 cycles of wood addition, using 25 wt. % 2-propanol in deionized water as the solvent and the same cobalt-molybdate catalyst. GC analysis indicated a yield of 78% of desired intermediates relative to the total amount of carbohydrates charged.

For Example 5, the experiment was repeated with 25% ethanol as the solvent, but with no catalyst. GC analysis indicated a yield of only 23% of the targeted intermediates, while 36% by weight of the wood feed was converted to a bottoms tar layer that could not be made to flow upon reheating to 100°C.

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 a to 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 referenced herein, the definitions that are consistent with this specification should be adopted.

CLAIMS

1. A biomass conversion system comprising:

a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first hydrocatalytic catalyst;

wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another;

a biomass feed mechanism that is operatively connected to the pressure vessel, the biomass feed mechanism being capable of introducing cellulosic biomass solids to the pressure vessel and also capable of withdrawing a reaction product from the first catalytic reduction reactor unit; and

a hydrogen feed line that is operatively connected to the first catalytic reduction reactor unit.

2. The biomass conversion system according to claim 0, wherein the pressure vessel comprises an annular structure, with the first section comprising an outer portion of the annular structure and the second section comprising an inner portion of the annular structure.

3. The biomass conversion system according to claim 1 or claim 2, wherein the first section and the second section are located alongside one another in the pressure vessel.

4. The biomass conversion system according to any one of claims 1 to 3, further comprising:

a fluid circulation loop establishing fluid communication between a fluid inlet of the pressure vessel and a fluid outlet of the biomass feed mechanism.

5. The biomass conversion system according to claim 4, wherein the fluid circulation loop further comprises a second catalytic reduction reactor unit that contains a second hydrocatalytic catalyst.

6. The biomass conversion system of claim 5, wherein the first catalyst and the second catalyst are the same.

7. The biomass conversion system according to claim 5, further comprising:

a solids separation mechanism located within the fluid circulation loop between the fluid outlet of the biomass feed mechanism and a fluid inlet of the second catalytic reduction reactor unit.

8. The biomass conversion system according to claim 5, further comprising:

a reaction product takeoff line in fluid communication with the fluid circulation loop, the reaction product takeoff line being located between the fluid inlet of the pressure vessel and a fluid outlet of the second catalytic reduction reactor unit.

9. The biomass conversion system according to any of the proceeding claims wherein the biomass feed mechanism is capable of introducing cellulosic biomass solids to the pressure vessel while the pressure vessel maintains a pressurized state;

and further comprise a fluid circulation loop comprising the pressure vessel and a second catalytic reduction reactor unit that contains a second hydrocatalytic catalyst.

10. The biomass conversion system according to claim 9, wherein the fluid circulation loop further comprises the biomass feed mechanism, the fluid circulation loop establishing fluid communication between a fluid inlet of the pressure vessel and a fluid outlet of the biomass feed mechanism.

11. The biomass conversion system according to claim 9, further comprising:

a solids separation mechanism located within the fluid circulation loop between a fluid outlet of the pressure vessel and a fluid inlet of the second catalytic reduction reactor unit.

12. The biomass conversion system according to claim 9, further comprising:

a reaction product takeoff line in fluid communication with the fluid circulation loop, the reaction product takeoff line being located between a fluid inlet of the pressure vessel and a fluid outlet of the second catalytic reduction reactor unit.

13. A method comprising:

providing a pressure vessel comprising a first section and a second section, the first section comprising a hydrothermal digestion unit and the second section comprising a first catalytic reduction reactor unit that contains a first hydrocatalytic catalyst;

wherein the hydrothermal digestion unit and the first catalytic reduction reactor unit are in fluid communication with one another;

adding cellulosic biomass solids to the pressure vessel;

heating the cellulosic biomass solids in the hydrothermal digestion unit of the pressure vessel, thereby forming a hydrolysate comprising soluble carbohydrates within a liquor phase;

conveying the liquor phase through the first catalytic reduction reactor unit in the presence of molecular hydrogen so as to at least partially transform the soluble carbohydrates into a reaction product; and

conveying at least a portion of the liquor phase from the pressure vessel to a second catalytic reduction reactor unit that contains a second hydrocatalytic catalyst, so as to further transform the soluble carbohydrates into the reaction product.

14. The method according to claim13, further comprising:

recirculating at least a portion of the liquor phase from the second catalytic reduction reactor unit to the pressure vessel.

15. The method according to claim 13 or claim 14, wherein the liquor phase is recirculated to the pressure vessel at a recycle ratio of 2 or less.

16. The method according to any one of claims 13 to 15, wherein at least 90% of the cellulosic biomass solids, on a dry basis, are digested to produce hydrolysate.

17. The method according to any one of claims 13 to 15, further comprising:

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

converting the reaction product into a biofuel.

18. The method according to any one of claims 13 to 17, wherein the first catalyst comprises a slurry catalyst.

19. The method according to claim 18, further comprising:

regenerating the slurry catalyst through exposure to water having a temperature of at least 200°C.

20. The method according to any one of claims 13 to 19, wherein the first section and the second section are located alongside one another in the pressure vessel.

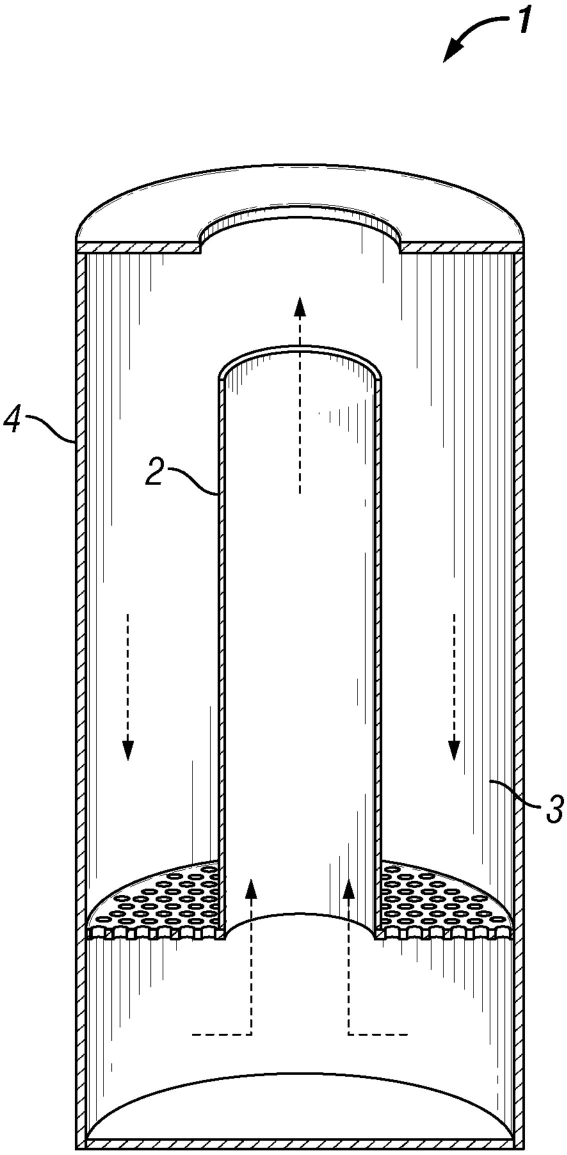

FIG. 1

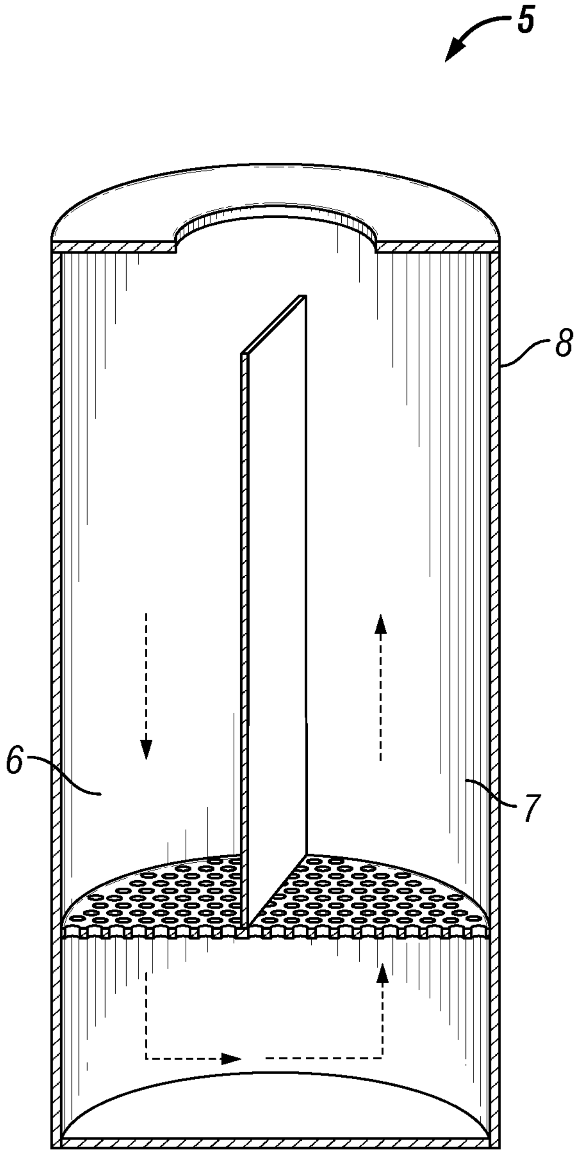

FIG. 2

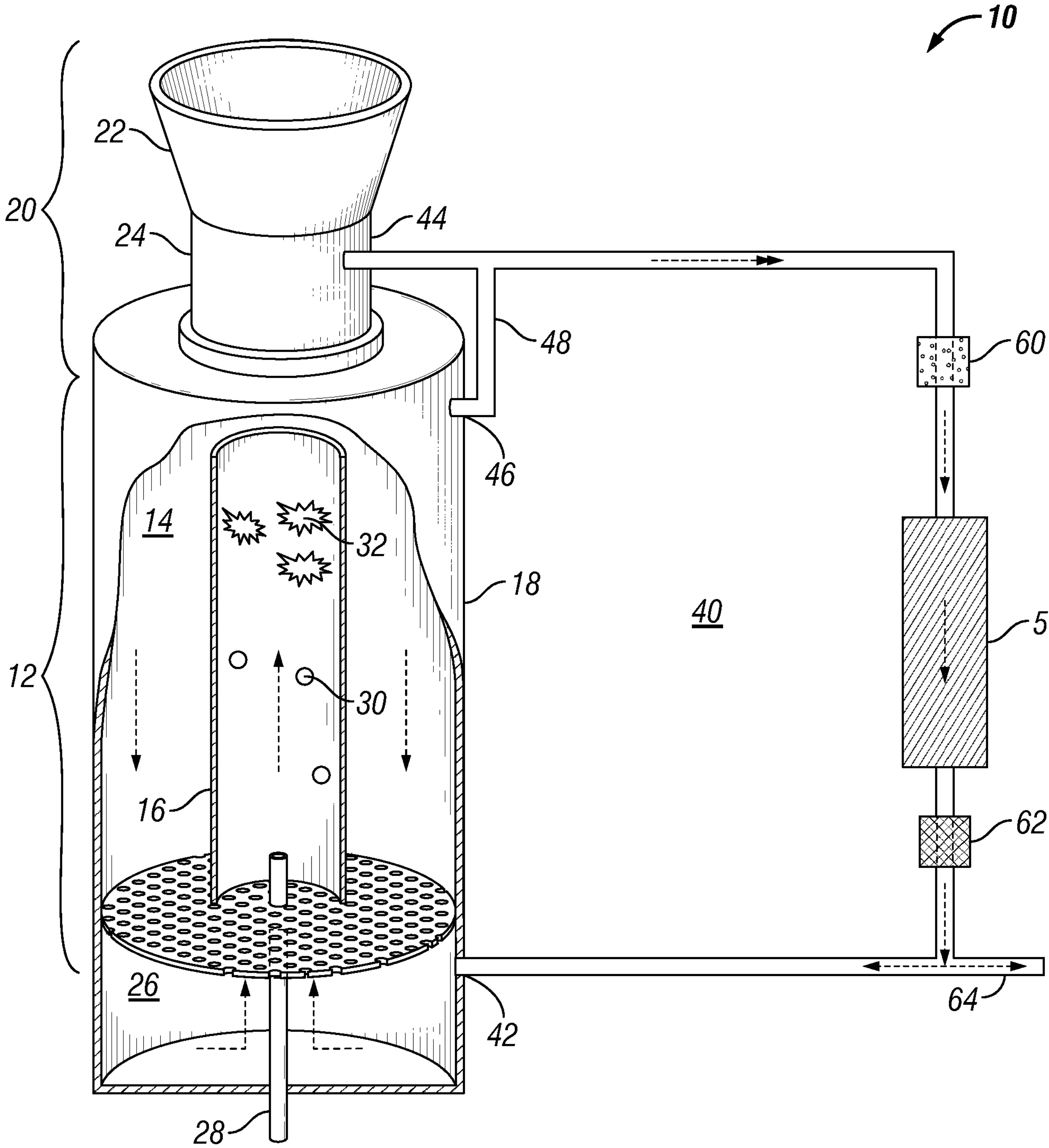

FIG. 3

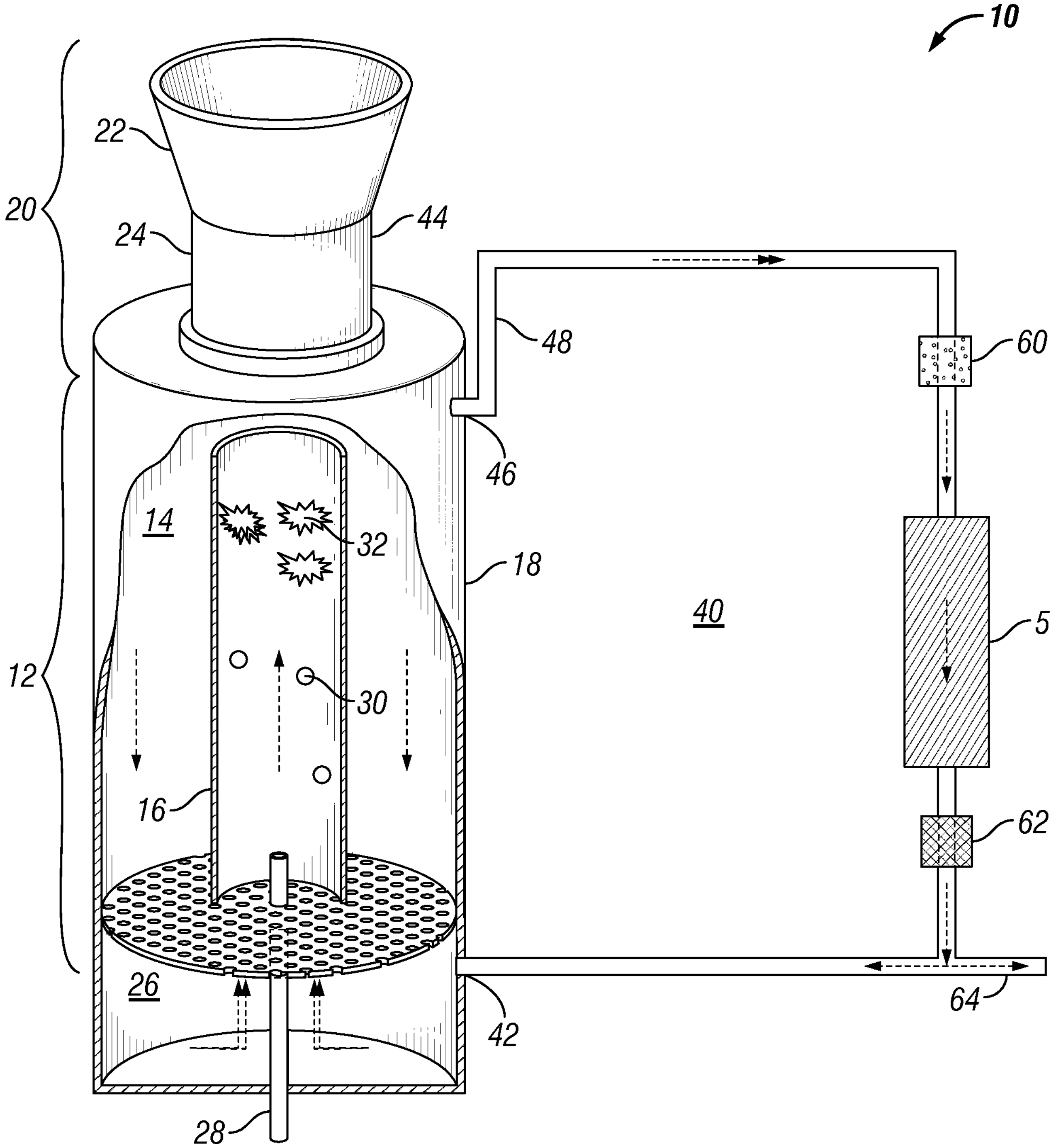

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/061561

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J3/00 C10G1/00 C10G1/06 C10G3/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C10G C10J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/151827 A1 (POWELL JOSEPH BROUN [US] ET AL) 21 June 2012 (2012-06-21) paragraphs [0013], [0025], [0031], [0039] - [0042], [0044], [0045], [0050] - [0054], [0057] - [0059], [0073], [0076], [0077] claim 1; figure 1 -----	1-20
X	US 5 421 998 A (LI LIXIONG [US] ET AL) 6 June 1995 (1995-06-06)	1-12
A	column 5, line 4 - column 6, line 13 column 7, lines 40-54 column 9, lines 28-38,47-68 figure 1 ----- -/--	13-20

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 17 December 2013	Date of mailing of the international search report 02/01/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Baumlin, Sébastien

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International application No
PCT/US2013/061561

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/139164 A1 (SOLRAY ENERGY LTD [NZ]; BATHURST CHRISTOPHER FRANCIS [NZ]) 10 November 2011 (2011-11-10) paragraphs [0056] - [0069] paragraph bridging pages 16 and 17 -----	1-20
A	US 5 500 120 A (BAKER DAVID L [US]) 19 March 1996 (1996-03-19) column 5, line 2 - column 6, line 14 figure 1 -----	1-20
A	US 2012/152836 A1 (POWELL JOSEPH BROUN [US] ET AL) 21 June 2012 (2012-06-21) the whole document -----	1-20

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/061561

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012151827 A1	21-06-2012	AU 2011349254 A1	11-07-2013
		CA 2822084 A1	28-06-2012
		CN 103415592 A	27-11-2013
		EP 2655558 A2	30-10-2013
		US 2012151827 A1	21-06-2012
		WO 2012088131 A2	28-06-2012
US 5421998 A	06-06-1995	AU 2436192 A	02-03-1993
		US 5421998 A	06-06-1995
		US 5454950 A	03-10-1995
		US 5527466 A	18-06-1996
		WO 9302969 A1	18-02-1993
WO 2011139164 A1	10-11-2011	CN 103221545 A	24-07-2013
		EP 2580339 A1	17-04-2013
		US 2013111807 A1	09-05-2013
		WO 2011139164 A1	10-11-2011
US 5500120 A	19-03-1996	NONE	
US 2012152836 A1	21-06-2012	AU 2011349336 A1	11-07-2013
		CA 2822105 A1	28-06-2012
		CN 103347984 A	09-10-2013
		EP 2655557 A2	30-10-2013
		US 2012152836 A1	21-06-2012
		WO 2012088121 A2	28-06-2012